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THE REACTION OF IRON PENTACARBONYL WITH SODIUM METHOXIDE

by

JUNE LYNCH McCLEAN

A dissertation submitted to the Graduate
Faculty in Chemistry in partial fulfillment of
the requirements for the degree of Doctor of Philosophy,
The City University of New York

1974

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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"I love the earth with all of myself."

Kahlil Gibran

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Abstract

THE REACTION OF IRON PENTACARBONYL WITH SODIUM METHOXIDE

by

June Lynch McClean

Adviser: Professor Bernard J. Bulkin

The reaction of iron pentacarbonyl with sodium methoxide in methanol and tetrahydrofuran solutions has been investigated in detail. Infrared and Raman spectroscopy, ^{1}H-NMR and chemical methods were used to study the products formed in this reaction. Contrary to previous thinking, the product is not a loose adduct, but the carbonyl inserted species.

Iron pentacarbonyl reacts with sodium methoxide at room temperature to produce the axially substituted species, $(CO)_4FeC(=O)OCH_3^-$.

$$Fe(CO)_5 + OCH_3^- \rightleftharpoons (CO)_4FeC(=O)OCH_3^-$$

A 1:1 mole ratio of reactants in methanol solution contains substantial amounts of both reactants and product. The equilibrium constant of the reaction is 1.2×10^2 L mole^{-1}. However, the reaction goes essentially to completion in

tetrahydrofuran solution.

In methanol solutions containing a large excess of sodium methoxide (1:14.5 mole ratio) the product reacts with a second mole of methoxide to produce a diaxially substituted species.

$$(CO)_4FeCOOCH_3^- + OCH_3^- \rightleftharpoons (CO)_3Fe(COOCH_3)_2^{2-}$$

The equilibrium constant for its formation is 6.7 x 10^{-1} L mole^{-1}. The second product does not form in tetrahydrofuran.

When $(CO)_4FeCOOCH_3^-$ is hydrolyzed with the stoichiometric amount of water, $HFe(CO)_4^-$ and the monomethyl carbonate ion, $CH_3OC(=O)O^-$, are formed.

$$(CO)_4FeC(=O)OCH_3^- + HOH \longrightarrow (CO)_4FeH^- +$$
$$CH_3OC(=O)O^- + H^+$$
$$H^+ + OCH_3^- \longrightarrow HOCH_3$$

The products are stable, but quite air sensitive. A few seconds of exposure to oxygen causes the pale yellow methanol solutions to turn deep red. The oxidation product is probably a polynuclear metal carbonyl. The oxidation product in THF solutions is $Fe(CO)_5$.

Heating a methanol solution of the products at 60° results in the production of more $(CO)_3Fe(COOCH_3)_2^{2-}$ at the expense of $(CO)_4FeCOOCH_3^-$. Thus, the formation of the second product is endothermic.

The infrared CO stretching frequencies of $(CO)_4FeCOOCH_3^-$ are 2030 (m), 1910 (s) and 1885 (m,sh) cm^{-1}. The Raman CO stretching frequencies are the same; those at 2030 and 1885 cm^{-1} are polarized, while the band at 1919 cm^{-1} is depolarized.

The number of bands, their relative intensities and their polarizations are consistent with an axially substituted trigonal bipyramid, for which three CO stretching bands are predicted ($2A_1 + E$).

In THF the infrared bands of the product are sharper and shifted to higher frequency. The depolarized (E) band is split, as expected for a complex with an unsymmetrical ligand. Thus, there are polarized bands at 2027 and 1905 cm^{-1}, and a depolarized pair of bands at 1930 and 1917 cm^{-1}.

Two additional bands are observed in the spectra of the THF solutions of $(CO)_4FeCOOCH_3^-$. These are at 1586 and 1413 cm^{-1}. The former band can also be seen in the spectra of methanol solutions (at 1590 cm^{-1}), while the latter is probably hidden under solvent absorption in methanol. The 1586 cm^{-1} band is assigned to the C=O stretch of the ligand, while the 1413 cm^{-1} band is probably a CH_3 deformation mode. Other ligand vibrations such as the C-O stretch are undoubtedly hidden by solvent absorption in both solvents.

The disubstituted product has a single CO stretching band at 1780 cm^{-1}. This is a broad band with a pronounced shoulder on the high wavenumber side. The low frequency of this band is due to the two units of negative charge. Only one infrared active CO stretching band, of representation E, is expected for a diaxially substituted trigonal bipyramid. The half width and shoulder on this band suggest that it is again split by the unsymmetrical ligands.

The ^1H-NMR spectra of $(CO)_3FeCOOCH_3^-$ in THF solution have a singlet at $\delta 3.5$ (downfield from TMS). In methanol solutions there is rapid exchange of $-OCH_3$ among methanol, free methoxide and the product. This results in a single peak for all the methyl protons. The peak is in the region of absorption of methoxy protons. Its exact position varies slightly with the concentration of methoxide and the product.

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INTRODUCTION

The Reactions of Metal Carbonyls with Nitrogen and Oxygen Bases

The reactions of metal carbonyls with Lewis bases have been of interest throughout the history of metal carbonyl research. The work has centered on the well-known and more easily obtained carbonyls, in particular those of vanadium, chromium, molybdenum, tungsten, manganese, iron, cobalt and nickel. The bases used were most often amines and aqueous or alcholic solutions of hydroxide. The classes of reactions found are disproportionations, substitutions and carbonyl insertions.

Disproportionations

The most common reaction type is the disproportionation of the metal carbonyl. The product is a salt in which the cation consists of a number of bases attached to a metal atom, and the anion is a metal carbonyl.

$$M_m(CO)_n + bB \longrightarrow [MB_b]\left[M_x(CO)_y\right]_z + n\text{-}yzCO \qquad (1)$$

The cation is always dipositive. With few exceptions it is hexacoordinate. Mononuclear anions are mononegative; polynuclear anions are dinegative.

Any CO groups not required for the anion are evolved as carbon monoxide. Disproportionations are found for all of the above metal carbonyls except those of the group VI metals: chromium, molybdenum and tungsten. The base is nearly always an amine or ammonia, but some disproportionations were reported with oxygen bases such as alcohols and water.

The first step in the disproportionation of the dinuclear metal carbonyls is probably the attack of one molecule of base resulting in cleavage of the carbonyl.

$$M_2(CO)_{2n} + B \longrightarrow M(CO)_nB^+ + M(CO)_n^- \qquad (2)$$

Initial products of this type have been found for a few of the disproportionation reactions. $[Co(CO)_4ROH][Co(CO)_4]$ and $[Co(CO)_4HOH][Co(CO)_4]$ were prepared from the carbonyl and the base at low temperature.[1] They are stable below 0°. The product, $[Co(CO)_4C_5H_{10}NH][Co(CO)_4]$, resulted from the reaction of $Co_2(CO)_8$ and piperidine at dry ice temperature.[2] Although the reaction of $Mn_2(CO)_{10}$ with strongly basic amines gave disproportionations (see below), there was one exception.[3] When the amine was n-butylamine, $[Mn(CO)_5C_4H_9NH][Mn(CO)_5]$ was formed. On this basis Hieber proposed the following mechanism for disproportionation of dimanganese decarbonyl:

$$[Mn(CO)_5]_2 \longrightarrow CO_5\overset{\delta+}{Mn}\text{-}\overset{\delta-}{Mn}CO_5 + B \longrightarrow [Mn(CO)_5B][Mn(CO)_5] \quad (3)$$

$$2Mn(CO)_5B^+ + 5B \longrightarrow MnB_6{}^{2+} + CO + e^- \quad (4)$$

$$[Mn(CO)_5]_2 + 2e^- \longrightarrow 2Mn(CO)_5 \quad (5)$$

In several papers Hieber and coworkers reported the valence disproportionation of dicobalt octacarbonyl resulting from reaction with a number of saturated and unsaturated amines.[4,5,6] In all reactions two moles of the tetracarbonylcobaltate(I) anion per mole of $Co_2(CO)_8$ were produced. The general reaction was:

$$3Co_2(CO)_8 + 2nB \longrightarrow 2[CoB_n][Co(CO)_4]_2 + 8CO \quad (6)$$

where n is 6, 3 or 2.

In each of these reactions carbon monoxide was generated. When the base was a saturated amine all or part of the CO formylated some of the amine. Reaction conditions were very mild. Dicobalt octacarbonyl and amines were condensed together and allowed to thaw. Other bases were stirred with $Co_2(CO)_8$ at room temperature.

When saturated amines with one nitrogen atom, such as pyrrolidine, morpholine, azirane and formylamine were used, cations resulted with six molecules of the base coordinated to the cobalt.

$$Co_2(CO)_8 + 6C_4H_{10}NH \longrightarrow Co(C_4H_{10}NH)_6{}^{2+} + 2\ Co(CO)_4{}^- \quad (7)$$

Unsaturated amines such as quinoline, α-and γ-picoline also gave this reaction. Diethylenetriamine, o-$C_6H_4(NH_2)_2$ and $(CH_3CNPh)_2$ were found to be bidentate, yielding $[CoB_3][Co(CO)_4]_2$ as the product. Both $NH(CH_2CH_2OH)_2$ and $N(CH_2CH_2OH)_3$ gave $[CoB_2][Co(CO)_4]_2$, indicating coordination through oxygen atoms as well as nitrogen. Other workers found a six coordinate cation with liquid ammonia[7] and dimethylamine.[8]

A few oxygen bases were investigated and these gave the disproportionation reaction. Wender and coworkers made $[Co(CH_3OH)_6][Co(CO)_4]_2$ and $[Co(CH_3CH_2OH)_6][Co(CO)_4]_2$ but did not isolate these products because removal of the solvent resulted in loss of the coordinatively bound alcohol.[2] Presumably a similar loss of coordinated base had occured in the formation[9] of disproportionation products containing the cations Co(acetophenone)$_{0.5}^{2+}$, Co(dioxane)$_{0.5}^{2+}$ and Co(benzophenone)$_{0.25}^{2+}$.

Reaction of $Co_2(CO)_8$ with water in benzene solution or with dilute aqueous alkali produced $[Co(HOH)_6][Co(CO)_4]_2$. The product was not isolated but the Co^{2+} was precipitated as $Co(OH)_2$ by addition of alkali.[2]

$$3Co_2(CO)_8 + 12H_2O \longrightarrow 2[Co(H_2O)_6][Co(CO)_4]_2 \qquad (8)$$

In strong alkali there is, in addition to disproportionation, the reduction of $Co_2(CO)_8$ and oxidation of carbon monoxide by hydroxide ion.[4]

$$8Co_2(CO)_8 + 8CO + 32OH^- \longrightarrow 16Co(CO)_4^- + 8CO_3^{2-} + 16H_2O \qquad (9)$$

The net equation is the sum of equations 8 and 9.

$$11Co_2(CO)_8 + 32OH^- \longrightarrow 2Co(H_2O)_6^{2+} + 20\ Co(CO)_4^- + 8CO_3^{2-} + H_2O \qquad (10)$$

More severe reaction conditions are required for the disproportionation of the manganese and iron carbonyls. Higher temperatures (20° to 120°) were employed. Sometimes the iron pentacarbonyl-base reaction mixtures were irradiated with ultraviolet light.

The disproportionations of iron pentacarbonyl and triiron dodecacarbonyl are very similar. Both result in ferrous cations and dinegative metal carbonyl anions. The anions are mono- or polynuclear depending on the base and the reaction temperature. While $Fe_4(CO)_{13}^{2-}$ and $Fe_2(CO)_8^{2-}$ were usually the anions in the final product, $Fe_3(CO)_{11}^{2-}$ could often be identified as a precursor. The number of monodentate nitrogen bases coordinated in the cation, where known, was six.

Hieber and Floss studied the reactions of $Fe(CO)_5$ and $Fe_3(CO)_{12}$ with phenanthroline and found that under identical conditions they gave the same products.[10] Both yielded the $Fe_2(CO)_8^{-2}$ anion, followed by $Fe_4(CO)_{13}^{-2}$ at higher temperature.

$$3Fe(CO)_5 + 3phen \xrightarrow[\text{pyridine}]{80^\circ} [Fe(phen)_6][Fe_2(CO)_8] + 7CO \qquad (11)$$

$$3Fe_3(CO)_{12} + 3phen \xrightarrow[\text{pyridine}]{80^\circ} [Fe(phen)_6][Fe_2(CO)_8] + 4CO \qquad (12)$$

$$5Fe(CO)_5 + 3phen \xrightarrow[\text{pyridine}]{100^\circ} [Fe(phen)_6][Fe_4(CO)_{13}] + 12CO \qquad (13)$$

$$5Fe_3(CO)_{12} + 3phen \xrightarrow[\text{pyridine}]{100^\circ} [Fe(phen)_6][Fe_4(CO)_{13}] + 21CO \qquad (14)$$

Triiron dodecacarbonyl in liquid ammonia yielded $[Fe(NH_3)_6][Fe_3(CO)_{11}]$. At higher temperatures the product reacts with more ammonia to give the $Fe_2(CO)_8^{2-}$ anion.[11]

$$3[Fe(NH_3)_6][Fe_3(CO)_{11}] + 6NH_3 \longrightarrow 4[Fe(NH_3)_6][Fe_2(CO)_8] + CO \qquad (15)$$

The $Fe_2(CO)_8^{-2}$ ion can also be produced at low temperatures (20°) by longer reaction times of 14 days.[12]

Iron pentacarbonyl and ammonia with pyridine as solvent gave $[Fe(NH_3)_6][Fe_2(CO)_8]$.[13]

In the presence of ultraviolet radiation iron pentacarbonyl reacts with pyridine at 40° to give the trinuclear anion. At reaction temperatures of 85° the tetranuclear anion is formed.[11]

$$4Fe(CO)_5 + xC_5H_5N \xrightarrow[3\ \text{days}]{h\nu\ \ 40^\circ} [Fe(C_5H_5N)_x][Fe_3(CO)_{11}] + 9CO \qquad (16)$$

$$[Fe(C_5H_5N)_x][Fe_3(CO)_{11}] \xrightarrow[Fe(CO)_5]{h\nu\ \ 85^\circ} [Fe(C_5H_5N)_x][Fe_4(CO)_{13}] \qquad (17)$$

At intermediate temperatures a mixture of the two products resulted.

Hieber and coworkers found that in the reaction of $Fe_3(CO)_{12}$ with ethylenediamine that the trinuclear anion is the first one formed. At higher temperatures other anions are produced.[14]

$$Fe_3(CO)_{12} \xrightarrow[40^\circ]{en} [Fe(en)_3][Fe_3(CO)_{11}] \xrightarrow{90^\circ} [Fe(en)_3][Fe_2(CO)_8] \xrightarrow{145^\circ} [Fe(en)_3][Fe(CO)_4] \qquad (18)$$

This differs from the phenanthroline reaction (above) in which $Fe_2(CO)_8{}^{2-}$ was converted to $Fe_4(CO)_{13}{}^{2-}$ at higher temperatures.

The reaction of iron pentacarbonyl with the saturated amines, piperidine, pyrrolidine and morpholine, at 80° yielded the $Fe_4(CO)_{13}{}^{2-}$ ion in the final product.[15] The piperidine and morpholine reactions gave an unusual cation. The formylated amine rather than the amine itself was coordinated to the iron.

$$5Fe(CO)_5 + 6OC_4H_8N \xrightarrow{80^\circ} [Fe(OC_4H_8NCHO)_6][Fe_3(CO)_{11}] \quad (19)$$

The same product was obtained by the reaction of $Fe(CO)_5$ and formylmorpholine. When the iron pentacarbonyl-morpholine reaction was carried out at higher temperatures the amine coordinated cation resulted.

The reaction of the iron carbonyls with oxygen bases is similar to the reaction with amines.[16] At 80° iron pentacarbonyl and dimethysulfoxide gave $[Fe(DMSO)_6][Fe_4(CO)_{13}]$, but triphenylphosphineoxide and triphenylarsineoxide gave unexpected coordination numbers, yielding $[Fe(Ph_3PO)_2][Fe_2(CO)_8]$ and $[Fe(Ph_3AsO)_3][Fe_2(CO)_8]$ respectively. Iron pentacarbonyl and pyridine-N-oxide did not give the disproportionation product. Instead, pyridine and ferric oxide were formed. However, the reaction $Fe_3(CO)_{12}$ and pyridine-N-oxide at room temperature gave $[Fe(C_5H_{10}NO)_6][Fe_4(CO)_{13}]$.

$Fe_3(CO)_{12}$ will react with alcohols even at low temperatures, while $Fe(CO)_5$ does not. After 5 days at 30° in ethyl alcohol the $Fe_3(CO)_{11}^{2-}$ ion was formed.[11]

$$4Fe_3(CO)_{12} \xrightarrow[CH_3CH_2OH]{30^\circ} [3Fe(CH_3CH_2OH)_x][Fe_3(CO)_{11}] + 15CO \qquad (20)$$

However, the $Fe_3(CO)_{11}^{2-}$ quickly reacts with alcohol to form $Fe_3(CO)_{11}H^-$ and $Fe(OC_2H_5)_2$. Concurrently, $Fe_3(CO)_{12}$ reacts with the carbon monoxide to form $Fe(CO)_5$. The overall reaction is:

$$6Fe_3(CO)_{12} \xrightarrow{C_2H_5OH} [Fe(C_2H_5OH)_x][Fe_3(CO)_{11}H]_2 + 10Fe(CO)_5 + Fe(OC_2H_5)_2 \qquad (21)$$

$Fe_3(CO)_{12}$ reacts in a similar manner with acetone.

$$6Fe_3(CO)_{12} \xrightarrow{acetone} [Fe(acetone)_x][Fe_3(CO)_{11}H]_2 + 10Fe(CO)_5 + Fe(OH)_2 \cdot aq \qquad (22)$$

The formation of the hydridocarbonyl anion is attributed by Hieber to the reaction of the initially formed $Fe_3(CO)_{11}^{2-}$

with traces of water in the acetone.

The disproportionation of $Mn_2(CO)_{10}$ proceeds by the following reaction:

$$3Mn_2(CO)_{10} + 2nB \longrightarrow 2\left[Mn(B)_n\right]\left[Mn(CO)_5\right]_2 + 10\ CO \qquad (23)$$

The number of coordinated bases, n, is 6, 3 or 2 depending on whether the ligand is mono-, bi- or tridentate. Disproportionation has been reported with amines that are relatively strong bases, such as piperidine, ethylenediamine, morpholine and pyridine.[3] The weaker bases, aniline and o-phenylenediamine gave substitution reactions (see below).

Like iron pentacarbonyl, nickel tetracarbonyl undergoes disproportionation with nitrogen bases to give a series of metal carbonyl anions.[17] When $Ni(CO)_4$ and pyridine react at 40° for 2 hours, the $Ni_2(CO)_6^{2-}$ ion is formed.

$$Ni(CO)_4 + 6\ py \longrightarrow \left[Ni(py)_6\right]\left[Ni_2(CO)_6\right] + 6CO \qquad (24)$$

The hexacarbonyldinickelate (I) ion reacted further to produce in sucession the anions $Ni_3(CO)_8^{2-}$, $Ni_4(CO)_9^{2-}$, and finally $Ni_5(CO)_9^{2-}$. The reaction can be reversed to $Ni(CO)_4$ by application of CO under pressure.[18]

The reaction of $Ni(CO)_4$ with γ-picoline, morpholine and piperidine gave $[Ni(B)_6][Ni_5(CO)_9]$. Hieber asserted that stronger bases stabilize the low nuclear anions, citing the reaction of $Ni(CO)_4$ with ethylenediame, a stronger base than pyridine.

$$Ni(CO)_4 + 6en \longrightarrow [Ni(en)_6][Ni_4(CO)_9] + 11CO \qquad (25)$$

A compound previously formulated as $Ni(phenanthroline)(CO)_2$ was revised to $[Ni(phen)_3][Ni_2(CO)_6]$.

Addition of acid to $Ni_2(CO)_9{}^{2-}$ results in the formation of the hydridocarbonyl, $Ni_4(CO)_9H^-$.

The disproportionation of $Ni(CO)_4$ with pyridine, morpholine, piperidine or picoline in the presence of water gave[17] $[Ni(B)_6][Ni_4(CO)_9H]_2$.

Vanadium hexacarbonyl reacts with Lewis bases according to the equation:

$$V(CO)_6 + nB \longrightarrow [V(B)_n][V(CO)_6]_2 + 6CO \qquad (26)$$

The metal atom in $V(CO)_6$ has 17 electrons, but the $V(CO)_6{}^-$ ion resulting from the disproportionation has the inert gas configuration. This results in high reactivity of $V(CO)_6$ toward weak Lewis bases. Disproportionation will occur with methanol, acetone, dioxane and di-n-butylether.[19]

These bases give a hexacoordinate cation. Hexacoordinate cations also result from the nitrogen bases pyridine, aniline, acetonitrile and benzonitrile.[19,20] As expected, N'-N-diphenylethylenediamine, o-phenthroline and o- and p-phenylenediamine were bidentate, giving products of the formula $[V(B)_3][V(CO)_6]_2$. However, α- and γ-picoline gave anomalous products, $[V(B)_4][V(CO)_6]_2$, where n=4 instead of 6. Triphenylphosphineoxide and dimethyl sulfoxide also did not fit the pattern, giving $[V(PPh_3PO)_4][V(CO)_6]_2$ and $[V(DMSO)_4][V(CO)_6]_2$. These cations do not have the same coordination numbers as they did in the analogous iron carbonyl product (above), which were 2 and 6 respectively.

Substitutions

The second type of metal carbonyl-base reaction is substitution, in which the base replaces one or more CO groups of the carbonyl. Whether a metal carbonyl-base reaction will be a substitution or a disproportionation depends on the nature of both the metal carbonyl and the base. Disproportionation is favored by a strong base and a relatively electronegative metal.

According to Hieber[3] the order of tendency to undergo disproportionation as opposed to substitution with

Lewis bases is

$$Cr < Mn < Fe < Co < Ni$$

The disproportionation of $Co_2(CO)_8$ proceeds at room temperature while heating is required for $Mn_2(CO)_{10}$, $Fe(CO)_5$ and $Fe_3(CO)_{12}$. $Cr(CO)_6$ has no disproportionation reactions.

This increase in disproportionation tendency parallels an increase in electronegativity of the metal. The metal carbonyl not included by Hieber in the series, $V(CO)_6$, is a special case because of the extra stability gained by the anion in achieving the inert gas electron configuration.

The tendency to substitution reactions increases with the "acceptor properties" of the base. Thus, good π-acceptors, such as phosphines, are well known for their substitution reactions with metal carbonyls. As the basicity of amines decreases, the reaction temperature required for the disproportionation of $Mn_2(CO)_{10}$ increases. With the weakest bases, only substitution occurs.

The majority of substitution reactions with Lewis bases is found for the carbonyls of the group VI metals: chromium, molybdenum and tungsten, which react according to the equation

$$M(CO)_6 + nB \longrightarrow M(CO)_{6-n}(B)_n + nCO \qquad (27)$$

Heating with excess carbonyl sometimes gives monosubstitution exclusively. Excess base favors di- and trisubstitution. Irradiating with ultraviolet light produces the monosubstituted product.[21]

Werner studied the rate of monosubstitution of molybdenum hexacarbonyl with amines and phosphines and found that the rate does not depend on the nature of the base or its concentration.[22] He proposed that cleaving of a CO from the carbonyl is the first and rate determining step of the mechanism.

$$Mo(CO)_6 \xrightarrow{h\nu} Mo(CO)_5 + CO \qquad (28)$$

$$Mo(CO)_5 + B \longrightarrow Mo(CO)_5B \qquad (29)$$

This mechanism was later extended to $Cr(CO)_6$ and $W(CO)_6$ as well.[23] The activation energies of the first step of these reactions agree with the respective activation energies of CO exchange of the metal carbonyls in the gas phase. The rate of further substitution was found to depend on the nature of the ligand.

Fowles and Jenkins obtained a monosubstituted product by heating excess chromium or molybdenum hexacarbonyl with morpholine.[24] With morpholine in excess, molybdenum or tungsten hexacarbonyl gave the disubstituted product. However, excess morpholine and chromium hexacarbonyl gave a mixture of the monosubstituted product and a solvent substituted (toluene) product.

$$Mo(CO)_6 + \text{excess } OC_4H_8N \xrightarrow{PhCH_3} Mo(CO)_4(OC_4H_8N)_2 \qquad (30)$$

$$Cr(CO)_6 + \text{excess } OC_4H_8N \xrightarrow{PhCH_3} Cr(CO)_5(OC_4H_8N) + Cr(CO)_3(PhCH_3) \qquad (31)$$

When the base was pyrrolidine a mixture of mono- and disubstituted products resulted. Excess carbonyl and piperazine gave the interesting product, $[Mo(CO)_5]_2(C_4H_8N_2)$, resulting from bonding through both nitrogen atoms. The authors were not able to make trisubstituted products by heating the metal carbonyl and amine, but they were able to replace toluene or mesitylene from a (π-arene)$Mo(CO)_3$ complex with morpholine or piperazine.

The compounds $Ph_2PCH_2CH_2N(CH_2CH_3)_2$, $PhP[CH_2CH_2N(CH_2CH_3)_2]_2$ and o-phenanthroline were bidentate, while $CH_3CH_2N(CH_2CH_2PPh_2)_2$ was tridentate.[25]

When ultraviolet irradiation was employed $W(CO)_6$ gave monosubstituted products with a diversity of amines, including aniline, p-bromoaniline, cyclohexylamine, dimethylamine and trimethylamine.[20]

A few substitution reactions have been found for $Mn_2(CO)_{10}$. With aniline and o-phenylenediamine the product[3] is $Mn(CO)_4B$. The reaction with o-phenanthroline differed from this however.[26] The carbonyl was not cleaved by this base.

$$Mn_2(CO)_{10} + \text{phen} \longrightarrow Mn_2(CO)_8(\text{phen}) + 2CO \qquad (32)$$

The infrared spectrum of the product indicates that it is $(CO)_5Mn\text{-}Mn(CO)_3\text{phen}$. A few seconds of ultraviolet radiation or even strong sunlight causes the product to cleave. Two $Mn(CO)_5$ radicals join to give $Mn_2(CO)_{10}$. The other product is $Mn(CO)_3\text{phen}$, which has an unpaired electron. It is likely that the aniline and o-phenylenediamine reactions proceed by this mechanism, without the necessity of strong light to cleave the metal carbonyl.

Substitution reactions have been found for nickel carbonyl. $Ni(CO)_4$ and liquid ammonia gave a mixture of compounds of the type $Ni(CO)_x(NH_3)_{4-x}$. These products were not isolated and were unstable above -60°.[27] Reaction at room temperature with pyridine gave the monosubstituted product, $Ni(CO)_3(py)$, which was not isolated but identified by its infrared spectrum.[18] Heating caused the product to disproportionate to $\left[Ni(py)_6\right]\left[Ni_2(CO)_6\right]$.

Reductions

A third group of metal carbonyl-base reactions is the reduction of the metal carbonyl; the metal carbonyl is converted to a carbonylmetallate ion. Reductions occur in reactions with hydroxide ion. The solvent is usually alcohol because, as suggested by Hieber, most metal carbonyls are not sufficiently soluble in aqueous medium to react to an appreciable extent.[4] Indeed, nickel tetracarbonyl,[28] chromium hexacarbonyl[29] and dimanganese octacarbonyl[30] are unchanged in aqueous alkali.

$Co_2(CO)_8$ reacts with aqueous alkali more slowly than with alcholic alkali and does not go to completion.[4] In strong alcholic alkali solutions, as discussed above, the reaction is a disproportionation by water accompanied by a reduction of $Co_2(CO)_8$ by hydroxide.

$$3Co_2(CO)_8 + 12HOH \longrightarrow 2\left[Co(HOH)_6\right]\left[Co(CO)_4\right]_2 + 8CO \qquad (33)$$

$$Co_2(CO)_8 + CO + 4\ OH^- \longrightarrow 2\left[Co(CO)_4\right]^- + CO_3^{2-} + 2HOH \qquad (34)$$

The net equation is:

$$11Co_2(CO)_8 + 32\ OH^- \longrightarrow 2Co(HOH)_6^{2+} + 8CO_3^{2-} + 20Co(CO)_4^- + HOH \qquad (35)$$

Thus, even though disproportionation does occur, most of the carbonyl is reduced to the tetracarbonylcobaltate ion.

Dimanganese decacarbonyl undergoes the same type of reaction as dicobalt octacarbonyl.[31] The overall equation is:

$$13Mn_2(CO)_{10} + 40\ OH^- \longrightarrow 2Mn^2 + 24MN(CO)_5^- + 10\ CO_3^{2-} + 2HOH \qquad (36)$$

Surprisingly, $Re_2(CO)_{10}$ did not react with hydroxide like $Mn_2(CO)_{10}$. Treatment with an alcoholic solution of KOH and water gave an anion that was suggested to have O and OH bridges.[32]

$$Re_2(CO)_{10} + 3KOH + HOH \xrightarrow[100^\circ]{alc} Re_2(CO)_8O_2H^- + K^+ + K_2CO_3 + H_2 + CO \qquad (37)$$

The hydrogen atom could not be removed from the product by a more concentrated solution of OH^-.

The iron carbonyls apparently do not undergo appreciable disproportionation by water because reaction with aqueous alkali solutions results in a simple reduction of the carbonyl. Iron pentacarbonyl reacts with aqueous hydroxide to give the hydridotetracarbonylferrate ion.[33]

$$Fe(CO)_5 + 3\ OH^- \longrightarrow HFe(CO)_4^- + HOH + CO_3^{2-} \qquad (38)$$

This ion is acidic and is converted to the tetracarbonylferrate(II) ion in strongly alkaline solution.[34]

$$HFe(CO)_4^- + OH^- \longrightarrow Fe(CO)_4^{2-} + HOH \qquad (39)$$

$Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ react in an analagous manner to give $Fe_2(CO)_8^{2-}$ and $Fe_3(CO)_{11}^{2-}$ respectively.[35]

While $Fe(CO)_5$ and NH_3 in pyridine solution give a disproportionation reaction (above), $Fe(CO)_5$ is reduced by liquid ammonia.[12]

$$Fe(CO)_5 + 4NH_3 \xrightarrow[\text{14 days}]{20^\circ} 2NH_4^+ + Fe(CO)_4^{2-} + CO(NH_2)_2 \qquad (40)$$

Diiron eneacarbonyl is reduced similarly.

$$Fe_2(CO)_9 + 4NH_3 \xrightarrow[\text{40 hours}]{20^\circ} 2NH_4^+ + Fe_2(CO)_8^- + CO(NH_2)_2 \qquad (41)$$

However, triirondodecacarbonyl gave a mixture of products.

$$Fe_3(CO)_{12} + 10NH_3 \xrightarrow[14\ days]{20^\circ} [Fe(NH_3)_6][Fe_2(CO)_8] + 2NH_4^+ + Fe(CO)_4^- + CO(NH_2)_2 + 3CO \qquad (42)$$

Since $Fe_3(CO)_{11}^{2-}$ is found in the solution when the reaction time is shorter, a mechanism is proposed involving the disproportionation of the metal carbonyl.[12]

$$Fe_3(CO)_{12} + 6NH_3 \longrightarrow [Fe(NH_3)_6][Fe_3(CO)_{11}] + CO \qquad (43)$$

$$[Fe(NH_3)_6][Fe_3(CO)_{11}] \longrightarrow [Fe(NH_3)_6][Fe_2(CO)_8] + Fe(CO)_5 \qquad (44)$$

The $Fe(CO)_5$ then reacts as in equation 40.

When nickel tetracarbonyl is treated with a saturated alcohol solution of NaOH for 80 hours the $Ni_3(CO)_8^{2-}$ ion results.[36] The yield was about 50%. What happened to the rest of the $Ni(CO)_4$ was not determined. Nor were any other products identified although there was a voluminous dark brown precipitate in addition to the solution containing the octacarbonyltrinicelate ion.

The carbonyls of the group VI metals are reduced by methanolic alkali to polynuclear anions containing hydroxo and methoxo groups. In ethanolic alkali anions containing hydroxo groups, but no ethoxo groups, are formed. Although the anions are similar, the reactions producing them are thought to be somewhat different for the three metal hexacarbonyls.

The reaction of $Cr(CO)_6$ with methanolic KOH was at first thought to give a mononuclear anion.[29,37] But further work showed it to be dinuclear.[38] The anion was said to vary between $[Cr_2(CO)_6(OH)_2(CH_3O)(H)]^{2-}$ and $[Cr_2(CO)_6(OH)(CH_3O)_2(H)]^{2-}$. Hydrogen, CO_3^{2-} and HCO_3^- were also produced. Ethanol solutions gave an anion containing no ethoxo groups, $[Cr_2(CO)_6(OH)_3(H)]^-$.

Molybdenum hexacarbonyl reacts with methanolic KOH at high temperature to give a dinuclear anion, but no carbonate or hydrogen were observed.[39] The anion contains a methoxo group.

$$2Mo(CO)_6 + 8OH^- \xrightarrow[90\text{-}120^\circ]{CH_3OH} [Mo_2(CO)_6(OH)_2(CH_3O)]^{3-} + 6HCOO^- \qquad (45)$$

In ethanol solutions, however, the anion contains only hydroxo groups, $[Mo_2(CO)_6(OH)_3]^{3-}$. When water is added to either of these anions, a third anion containing a hydrido group is formed, $[Mo_2(CO)_6(OH)_3H]^{2-}$.

Tungsten hexacarbonyl appears to have two reactions with methanolic HOH, resulting in a mixture of two anions.[40] One reaction gives a product analagous to the molybdenum anion above except for an additional hydrogen atom.

$$2W(CO)_6 + 8\ OH^- \xrightarrow[80\text{-}100^\circ]{CH_3OH} [W_2(CO)_6(OH)_2(CH_3OH)_2]^{2-} + HCOO^- \qquad (46)$$

The other reaction is a reduction like that of chromium hexacarbonyl.

$$2W(CO)_6 + 12\ OH^- \xrightarrow[80\text{-}100^\circ]{CH_3OH} [W_2(CO)_6(OH)_2(CH_3OH)_2]^{4-} + H_2 + 2CO_3^{2-} + 4HCOO^- + 2HOH \qquad (47)$$

At higher temperatures a trinuclear anion is formed, $[W_3(CO)_9(OH)(OCH_3)(CH_3OH)(H)]^{3-}$. With ethanol as solvent the two anions that are formed are $[W_2(CO)_6(OH)_3]^{3-}$ and $[W_2(CO)_6(OH)_3(H)]^{4-}$.

Carbonyl Insertions

There is a small group of metal carbonyl-base reactions in which a molecule of base becomes bonded to one of the CO groups of the metal carbonyl.

$$M(CO)_n + B \longrightarrow (CO)_{n-1}MC(=O)B \qquad (48)$$

The first such reaction to be found was the reaction of iron pentacarbonyl with saturated amines under mild conditions (room temperature or below). Other reactions were proposed for these compounds before a carbonyl insertion reaction was conclusively shown to take place.

The reaction of iron pentacarbonyl with amines under mild conditions was thought by Hieber to give a loose addition product.[15] Iron pentacarbonyl and piperidine or pyrrolidine were condensed together in a flask, evacuated and thawed. The yellow crystals that formed were found by elemental analysis to have the formulas $Fe(CO)_5 \cdot 3C_5H_{10}NH$ and $Fe(CO)_5 \cdot 2C_4H_8NH$. These products are stable only below 0°. Heating causes the products to disproportionate to $[Fe(C_5H_{10}NCHO)_6][Fe_4(CO)_{13}]$ and $[Fe(C_4H_8NH)_6][Fe_4(CO)_{13}]$ respectively. No explaination was offered for the coordination of formylamine in the one case and not the other.

When dissolved in a non-polar solvent the products gave the spectrum of the amine and unmodified $Fe(CO)_5$. This was explained by formulating the products as loose adducts, in which the primary coordination sphere of the iron is undisturbed.

Sternberg and coworkers observed that when iron pentacarbonyl is dissolved in amines no CO evolution is observed.[41] The resulting solution has a measurable conductivity and two bands in the carbonyl stretching region. On this basis they proposed that $Fe(CO)_5$ disproportionates in the amine for form $Fe(CO)_6^{2+}$ and $Fe(CO)_4^{2-}$. One infrared band was assigned to each ion, the higher frequency band to the cation.

Later Edgell and coworkers found that the loose adduct and the disproportionation proposals are incorrect.[42,43] Detailed spectroscopic and conductance studies showed that the initial product of a reaction of $Fe(CO)_5$ with excess amine is an amide substituted iron tetracarbonyl resulting from the attack of the amine on a carbonyl carbon.

$$Fe(CO)_5 + C_5H_{10}NH \longrightarrow (CO)_4FeC(=O)NHC_5H_{10} \qquad (49)$$

The amine hydrogen atom is in equilibrium between the product and another amine molecule, hence the observed conductivity of the solutions.

$$(CO)_4FeC(=O)NHC_5H_{10} + HNC_5H_{10} \longrightarrow (CO)_4FeC(=O)NC_5H_{10}^- \quad H_2NC_5H_{10}^+ \qquad (50)$$

These products were not isolated. However, Hieber's piperidine product, when dissolved in excess piperidine, was found to be identical to Edgell's amide substituted compound. The reaction has only a moderate equilibrium constant. Thus, when the "adduct" was dissolved in a non-polar solvent it reverted to the reactants, $Fe(CO)_5$ and amine.

Over a period of a few days, or a few hours with heating, $(CO)_4FeC(=O)NC_5H_{10}^-$ was converted to an amine substituted iron tetracarbonyl, $(CO)_4FeNC_5H_{10}^-$. N-formylated amine was also produced. Thus, the reaction was called an insertion of a carbonyl group between the hydrogen and nitrogen of the amine.

Hydrolysis of the initial product, $(CO)_4FeC(=O)NC_5H_{10}^-$, gave $(CO)_4FeH^-$ and the piperidine carbamate ion, $C_5H_{10}NCOO^-$.

Other carbonyl insertion reactions have been found since the iron carbonyl-amine work was done. When the azide ion reacts with $Cr(CO)_6$, $Mo(CO)_6$ or $W(CO)_6$ the result is not the substituted product but an anion containing the isocyanate group.[44]

$$M(CO)_6 + N_3^- \xrightarrow[\text{diglyme}]{80^\circ} M(CO)_5NCO^- \qquad (51)$$

The azide ion is thought to attack a carbonyl group and the rearrange with loss of N_2 in a manner analogous to the

Curtius azide degradation. The same product results from the reaction of $W(CO)_6$ with KNCO.[45]

Primary amines have been found to react with substituted manganese and rhenium carbonyl cations. The amine attacks one of the carbonyl carbons yielding a neutral amide substituted compound. One of the amine hydrogens is taken up by a second amine molecule.[46]

$$\text{(hexamethylbenzene)}Mn(CO)_3^{+} + 2RNH_2 \longrightarrow \text{(hexamethylbenzene)}Mn(CO)_2NHR + RNH_3^{+} \qquad (52)$$

The cation $(RHN)_3Mn(CO)_3^{+}$ did not react. Electron donating ligands make the carbonyl carbon less positive and therefore less susceptable to attack.

Rate studies were done for reactions of the type.

$$M(CO)_4(L)_2^{+} + 2RNH_2 \longrightarrow t\text{-}M(CO)_3(L)_2CONHR + RNH_3^{+} \qquad (53)$$

M = Mn or Re and L = PPh_3, $P(Ph)_2CH_3$ or $PPh(CH_3)_2$

The rate equation was found to be the following:

$$\text{rate} = \left[k\ M(CO)_4L_2^{+}\right]\left[RNH_2\right]^2$$

This was interpreted as indicating a base catalyzed amine attack at a carbonyl carbon.[47] The second amine attacks a hydrogen of the first, thereby promoting the attack of the first amine on the carbonyl.

The Iron Pentacarbonyl-Methoxide Reaction

The reaction of iron pentacarbonyl with sodium methoxide and sodium ethoxide was also said to give a loose adduct.

$$Fe(CO)_5 + NaOCH_3 \longrightarrow Fe(CO)_5{\cdot}NaOCH_3 \qquad (54)$$

Hock and Stuhlman claimed that this adduct could react with more methoxide to give dimethylcarbonate and an ionic sodium iron tetracarbonyl.[48]

$$Fe(CO)_5{\cdot}NaOCH_3 + NaOCH_3 \longrightarrow Na_2Fe(CO)_4 + CO(OCH_3)_2 \qquad (55)$$

Feigl and Krumholz said that the adduct reacts with water and additional methoxide in ether solution to give sodium methylcarbonate and a metal carbonyl compound that could be written as either $Fe(CO)_4H_2{\cdot}NaOCH_3$ or $Fe(CO)_4{\cdot}NaH{\cdot}CH_3OH$. The authors preferred the latter formula because heating the isolated compound in a vacuum caused the compound to release a large amount of methanol.[49]

Interestingly, Hieber asserted that iron pentacarbonyl does not react with methoxide at all unless traces of water are present.[50]

$$Fe(CO)_5 + NaOCH_3 + HOH \longrightarrow H_2Fe(CO)_4 + CH_3OC(=O)ONa \qquad (56)$$

These conflicting reports indicate a need for more work on the iron pentacarbonyl-methoxide reaction, especially in view of the demise of the loose adduct proposal in the iron pentacarbonyl-amine case. Furthermore, the alkoxide ion was found to react with a number of substituted metal carbonyl cations to give compounds of the form $M(CO)_nL_mC(=O)OR$.[51] The metals were manganese, rhenium, iron, osmium, cobalt, rhuthenium and iridium. The ligands included PPh_3, $SbPh_3$ and C_5H_5.

Conclusive knowledge of the iron pentacarbonyl-methoxide reaction can further understanding of all iron pentacarbonyl-base reactions, in particular those occuring under mild conditions.

This thesis is a study of the room temperature reaction of iron pentacarbonyl with sodium methoxide in methanol and tetrahydrofuran solutions. A great deal of information about the products of the reaction is obtained from their infrared and Raman spectra, especially in the carbonyl stretching region. This is supplemented and reinforced by ^{1}H-NMR spectra and chemical evidence.

The hydrolysis of the products is investigated in detail and furnishes further evidence for the nature of the products. The stability, oxidation products and effect of higher temperature (60°) are also discussed.

EXPERIMENTS AND RESULTS

Chemicals

The iron pentacarbonyl purchased from Antara Chemical is 99.9% pure. It will slowly decompose, but the iron and carbon monoxide that are produced are not soluble in the carbonyl and present no difficulties. Other workers have shown that impurities in iron pentacarbonyl are negligible and that it can be used as purchased without further purification.[52]

MCB Spectroquality methanol, guaranteed to contain a maximum of 0.05% water, was further dried by either of the following procedures. About 200 ml of the methanol were stored overnight over fresh Davison 3A molecular sieves in the apparatus pictured in figure 1. The methanol was freeze deaerated and distilled _in vacuo_ onto fresh molecular sieves. The alternative procedure involved refluxing the Spectroquality methanol over magnesium in the presence of a trace of iodine.[53] This was followed by distillation and freeze deaeration. Finally, in both procedures, the vacuum line and apparatus were filled with nitrogen. The flask

Figure 1

Apparatus for deaerating and distilling methanol

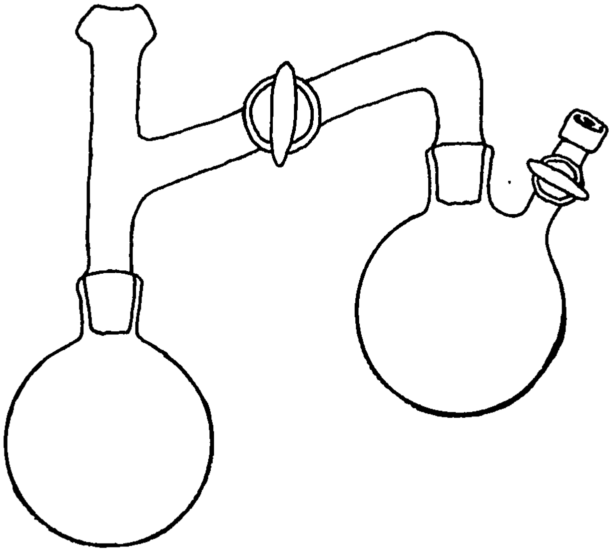

Figure 1

containing the dry methanol was detached while a brisk flow of nitrogen was blown in through its sidearm. The flask was quickly stoppered with a stopcock and ball joint adapter (figure 2). Portions of methanol could be removed as needed by syringe needle inserted through the serum stopple cap of the adapter.

The sodium methoxide was purchased from Aldrich as a 25% solution in methanol (4.3 M). It was freeze deaerated. Sodium methoxide was also prepared by the reaction of high purity sodium from Alfa Inorganics, 99.95% pure, with deaerated methanol. The sodium came in a glass tube with a break seal. The tube was sealed onto the bottom of a flask fitted with a ball joint adapter. The flask was evacuated on a vacuum line, the break seal opened, and methanol added via a syringe needle inserted through a serum stopple capped side arm. The flask was opened to a mercury bubbler to release the pressure of the hydrogen generated by the reaction. While the reaction was vigorous at first, it slowed as the solution became viscous with methoxide. After several days the reaction was still proceeding very slowly. The sodium methoxide solution that had been produced up to that time was removed by syringe. It was found to be 6.0 N by titration with aqueous HCl to a

Figure 2

Storage flask for methanol and sodium methoxide solutions

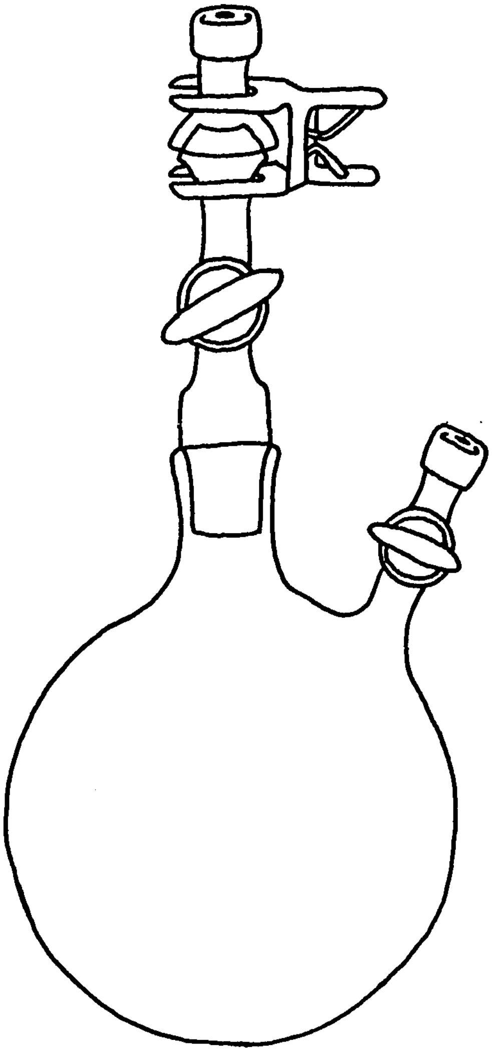

Figure 2

phenolphthalein end point. Since this high purity methoxide gave the same results in experiments as that from Aldrich the latter was used because of its convenience.

Tetrahydrofuran (Aldrich) was dried by overnight storage over $LiAlH_4$ followed by distillation and freeze deaeration.

Water and n-hexane were required in amounts of 5 ml or less, hence they were deaerated just prior to use. Fischer n-hexane was stored overnight over 3A molecular sieves. The hexane and water were deaerated by bubbling nitrogen through them while warming in a bath. This deaeration procedure is suitable and convenient for the small amounts of these liquids used.

Tetraphenylarsonium chloride was purchased from J. T. Baker Chemical Company and was used without further purification.

Sodium methylcarbonate was prepared by bubbling CO_2 through a solution of sodium methoxide in methanol[54]

$$CO_2 + NaOCH_3 \longrightarrow NaOC(=O)OCH_3 \qquad (57)$$

The white solid formed quickly. It was washed and dried. It was necessary to exclude moisture because water will hydrolyze the monomethylcarbonate to sodium hydrogen carbonate.

Sodium carbonate, sodium hydrogen carbonate, sodium acetate, and sodium formate were purchased as reagent grade chemicals and were used without further purification.

Matheson nitrogen was tested and found to be sufficiently dry by bubbling it through an ether solution of sodium benzophenone ketyl at a rate of about 5 cm^3/sec. After half an hour the blue color of the ketyl was still present. However, it is wise to test each cylinder of nitrogen in this manner since it is possible for a particular cylinder to be contaminated.

Precautions against Oxygen, Water and Light

The iron carbonyl derivatives discussed herein were found to be extremely sensitive to oxygen and moisture. Hence all operations were of necessity carried out *in vacuo* or under nitrogen. Since the compounds were often studied in dilute solution (about 0.2 M) the concentration of water had to be substantially less than 0.2 M. This is the reason for the careful drying procedures described above. All glassware and syringe needles were baked to dryness in an oven, quickly assembled and cooled in a stream of nitrogen. Reactions were usually carried out in centrifuge tubes snugly fitted with a serum stopple. The capped tubes were flushed with nitrogen for thirty minutes before use by means of syringe needles through the stopple.

Samples of liquids were withdrawn by syringe by inserting the syringe needle through the serum stopple. A second needle connected by hose to a nitrogen cylinder insured that pressure in the tube was equalized without the admission of air. Although serum stopples do close up after being punctured, if the sample is to be preserved for more than a day it is best to cover the top of the serum stopple with some sort of sealing material. It was found that a volatile solvent will evaporate from a tube capped with an unpunctured serum stopple if left for several weeks. Covering the stopple is especially important if many samples are taken; many punctures reduce the ability of the serum stopple to reseal. For this purpose silicone adhesive was found to be ideal. It is easy to apply and peels off easily when hard.

Airfree transfers of liquids from one tube to another were accomplished by the double-ended needle technique. A double-ended needle is the metal tube of a syringe needle, sharpened at both ends. One end is below the surface of the liquid; the other end is in the empty tube (figure 3). A flow of nitrogen entering the tube

Figure 3

Airless transfer of liquids by the double-ended needle technique

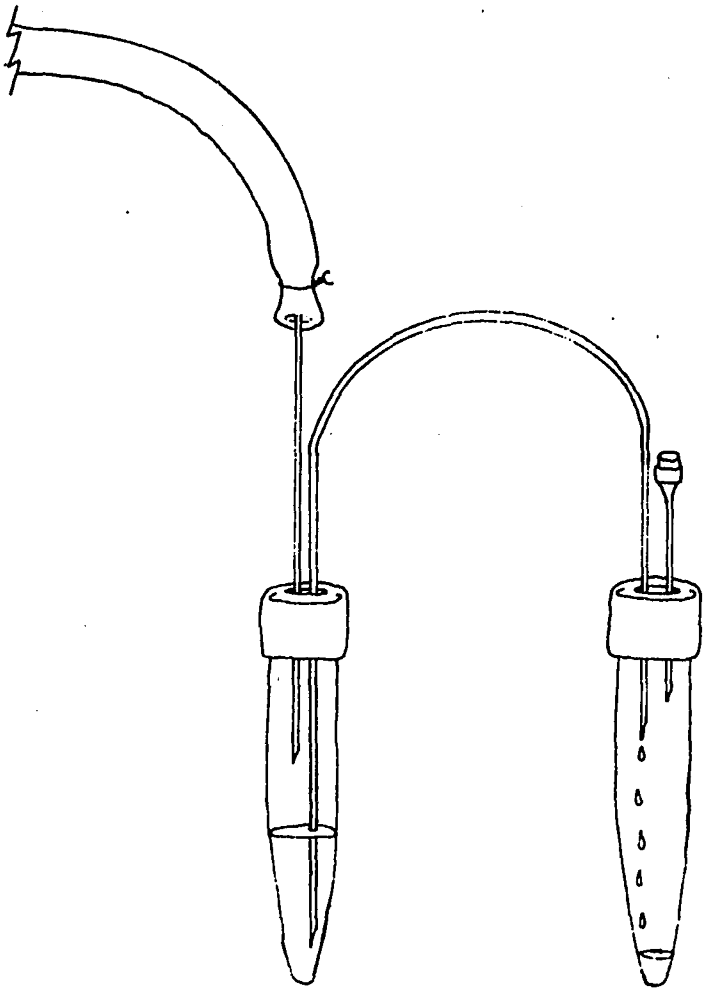

Figure 3

through a syringe needle forces the liquid through the double-ended needle into the empty tube. Another syringe needle through the serum stopple of the empty tube releases the pressure. Occasionally reactions were carried out on a vacuum line for a particular purpose. Special glassware, such as the methanol distillation apparatus, was designed and constructed as the need for it arose. Operations such as the collection of crystals and the preparation of Nujol mulls were done in a glove bag made by Instruments for Research and Industry.

Spectra of mulls were taken with NaCl and KBr windows. Beckman demountable cells with IRtran windows and Teflon spacers were used for liquid infrared samples. These cells are easily disassembled for cleaning. Also, the path length can be varied to suit the sample; usually 0.015 mm spacers were used because the CO stretching bands of metal carbonyls are very intense. The cell was filled by placing it in a plastic bag connected by hose to a cylinder of nitrogen. The bag was purged several times and the cell flushed with nitrogen. Syringes were also flushed with nitrogen by filling them several times from the bag. The cell was filled by inserting the syringe needle through the bag into the port of the cell and letting the liquid run in the cell.

NMR tubes were filled in a glove bag. The caps were sealed to the tubes with a small amount of silicone adhesive. Samples sealed in this manner were found to last for several days.

Because iron carbonyl derivatives are often decomposed by light it was assumed that the compounds studied herein were also somewhat light sensitive. No change in the color of solutions or the intensity of infrared absorption bands was observed with the moderate exposure to light during the manipulation of the compounds. However, the compounds were stored in containers covered with aluminum foil as a precaution.

Instruments

Infrared spectra were taken on the Perkin Elmer 521. The spectrometer was calibrated using HCl, DCl and atmospheric absorption bands as reference frequencies. Raman spectra were taken on the Spex Industries Model 1401. The 632.8 nm line of the Spectra Physics Model 125 He-Ne laser was used as the exciting line. The power at the sample was 50 mW. Several other emission lines of a Kr^+ ion laser were attempted for higher power excitation of the sample, but all led to photodecomposition. The Varian A-60 was used for the proton magnetic resonance spectra.

Infrared Spectra of Methanol Solutions

Much of the evidence concerning the products of the reaction of iron pentacarbonyl with sodium methoxide was obtained from the infrared spectra in the 2000 cm^{-1} region, where the metal carbonyl CO stretching modes absorb. This is an excellent probe because the frequencies and intensities of the bands are quite sensitive to the nature of other ligands bound to the metal atom, and the symmetry of the metal carbonyl moiety as a whole.

Another important advantage as a diagnostic is that the CO stretching vibrations are not coupled to other vibrations of the molecule. The metal-carbon stretching vibrations, on the other hand, are strongly coupled with the metal-carbon-oxygen bending modes. This makes it quite difficult to assign bands in the low wavenumber region of the spectrum, where these modes absorb. However, the extensive coupling makes this region unique for every molecule. Thus, a compound can be identified if its spectrum matches that of a known compound.

The carbonyl stretching frequencies of iron pentacarbonyl are solvent dependent. A spectrum of a 0.15 M solution of $Fe(CO)_5$ in methanol has bands at 2020 cm^{-1} and

2000 cm^{-1} (figure 4). Figures 5 and 6 are spectra of methanol and the solution of sodium methoxide in methanol respectively.

0.35 ml of the stock sodium methoxide solution from Aldrich was dissolved in 5.0 ml of methanol. 0.20 ml of iron pentacarbonyl was added and the tube shaken for about a minute to dissolve the carbonyl. This is a 1:1 mole ratio of $Fe(CO)_5$ to OCH_3^- in 0.30 M solution. An infrared spectrum taken within two minutes of mixing shows that a reaction has taken place. As seen in figure 7 the bands of $Fe(CO)_5$ are still present, but a new band appears at 1910 cm^{-1} with a shoulder at 1885 cm^{-1}. When reactions are carried out with higher mole ratios of OCH_3^- to $Fe(CO)_5$, the bands of unreacted $Fe(CO)_5$ become weaker and the new bands become more intense. At a mole ratio of 1:7 $Fe(CO)_5$ to methoxide the bands of iron pentacarbonyl are completely gone and the bands of the product are fully grown in. Figure 8 shows the spectrum of the product free of the bands of $Fe(CO)_5$. Bands are seen at 2030 cm^{-1} (medium), and 1910 cm^{-1} (strong) with a strong-medium shoulder at 1885 cm^{-1}. Spectra taken at intervals of 15 minutes to several days after mixing show no change in the intensity of the bands. Hence, equilibrium in these solutions is

Figure 4

Infrared spectrum of $Fe(CO)_5$ in methanol

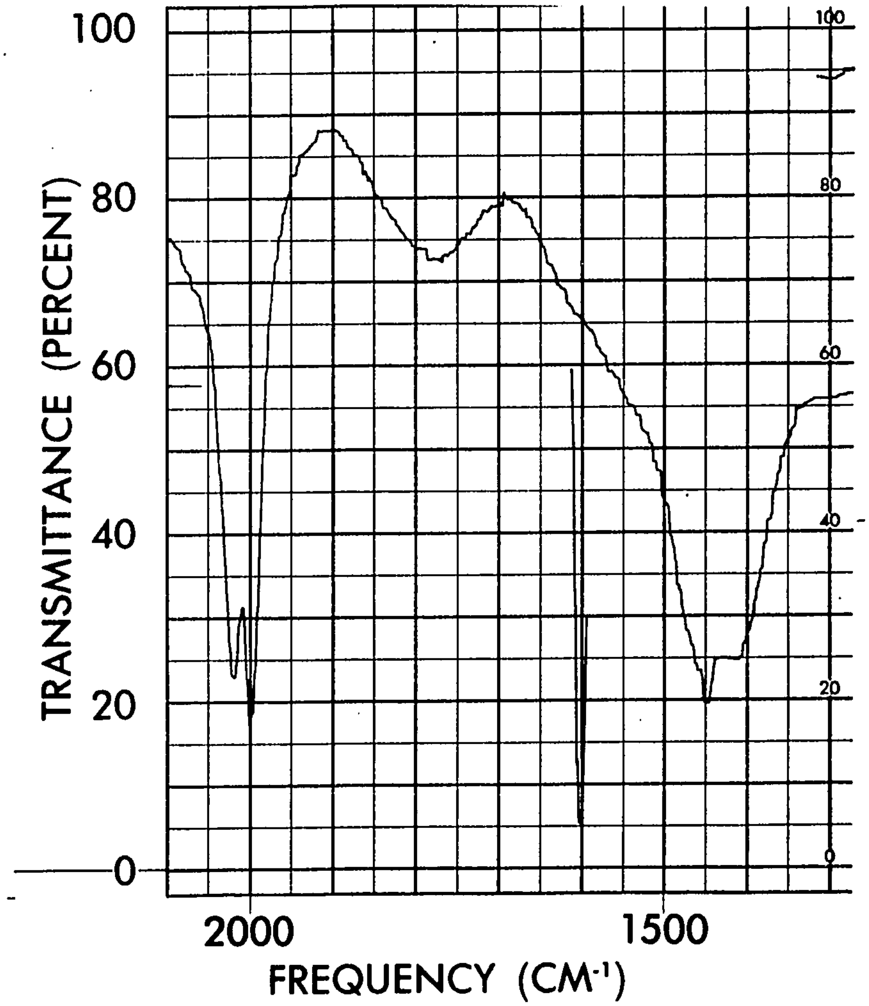
TRANSMITTANCE (PERCENT)
100
80
60
40
20
0
2000
1500
FREQUENCY (CM⁻¹)
100
80
60
40
20
0

Figure 4

Figure 5

Infrared spectrum of methanol

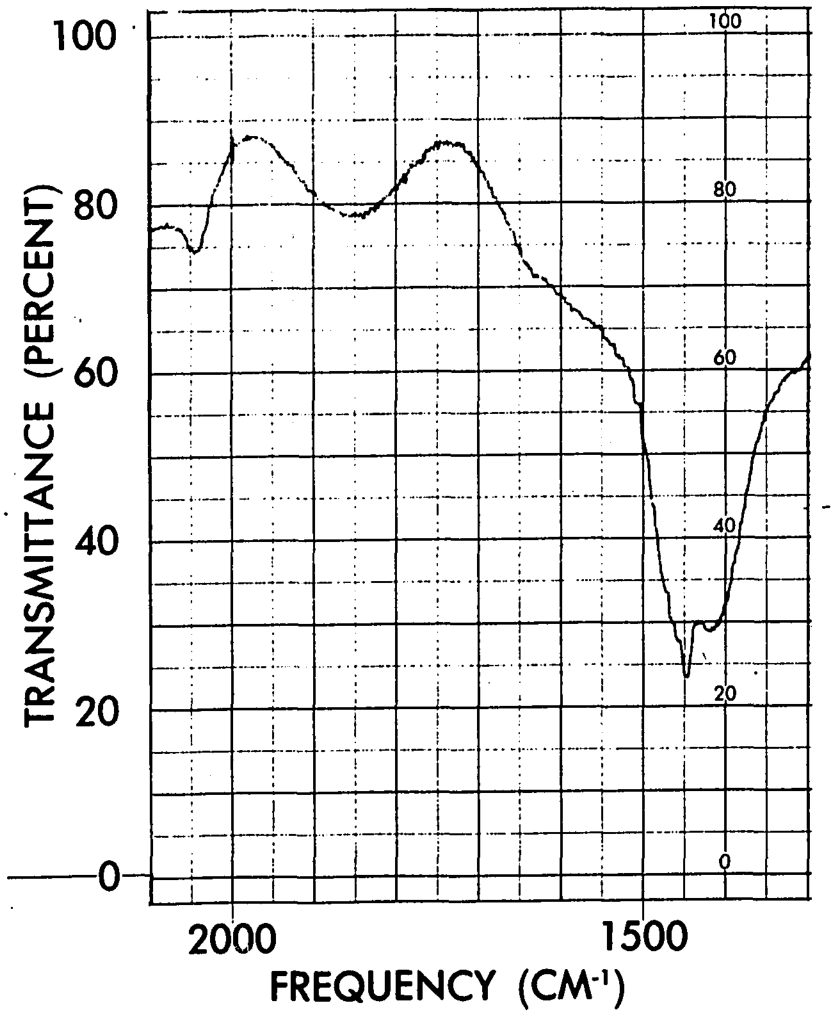
100
80
60
40
20
0
100
80
60
40
20
0
TRANSMITTANCE (PERCENT)
2000
1500
FREQUENCY (CM-1)

Figure 5

Figure 6

Infrared spectrum of $NaOCH_3$ in methanol

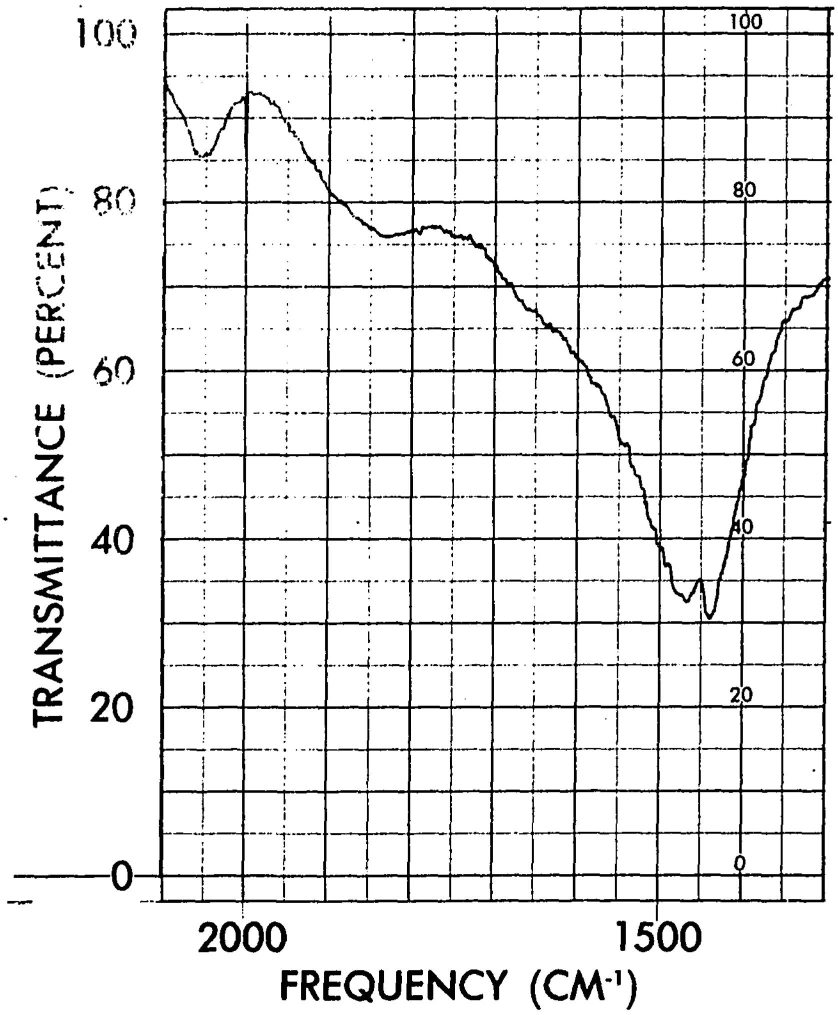
100
80
60
40
20
0
100
80
60
40
20
0
TRANSMITTANCE (PERCENT)
2000
1500
FREQUENCY (CM-1)

Figure 6

Figure 7

Infrared spectrum of a 1:1 mole ratio of $Fe(CO)_5$ and $NaOCH_3$ in methanol

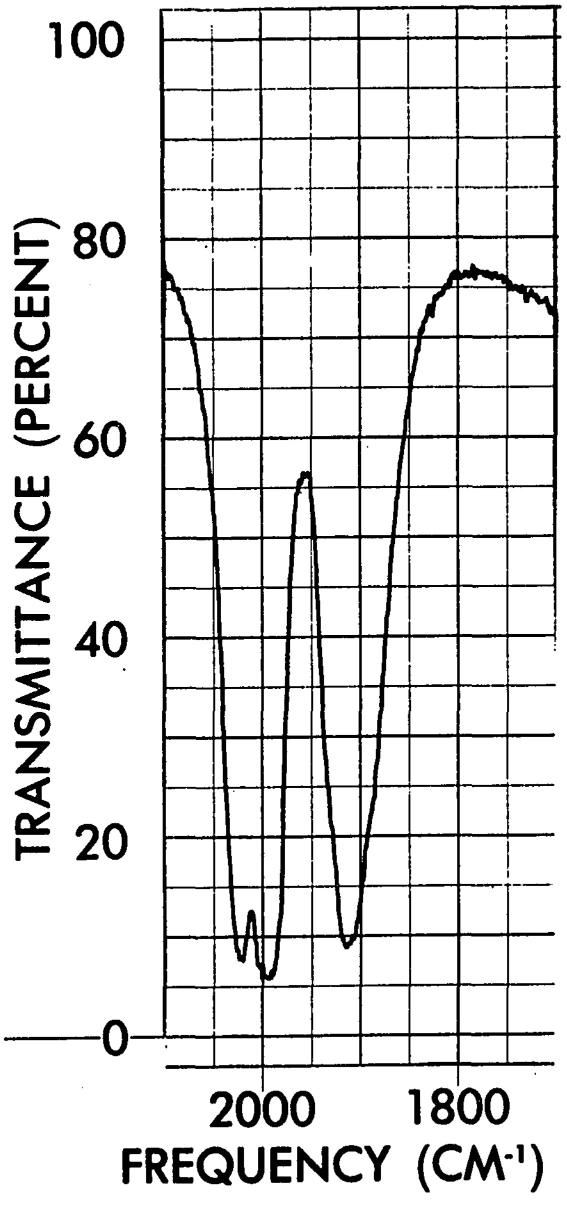
100
80
60
40
20
0
TRANSMITTANCE (PERCENT)
2000
1800
FREQUENCY (CM-1)

Figure 7

Figure 8

Infrared spectrum of a 1:7 mole ratio of $Fe(CO)_5$ and $NaOCH_3$ in methanol

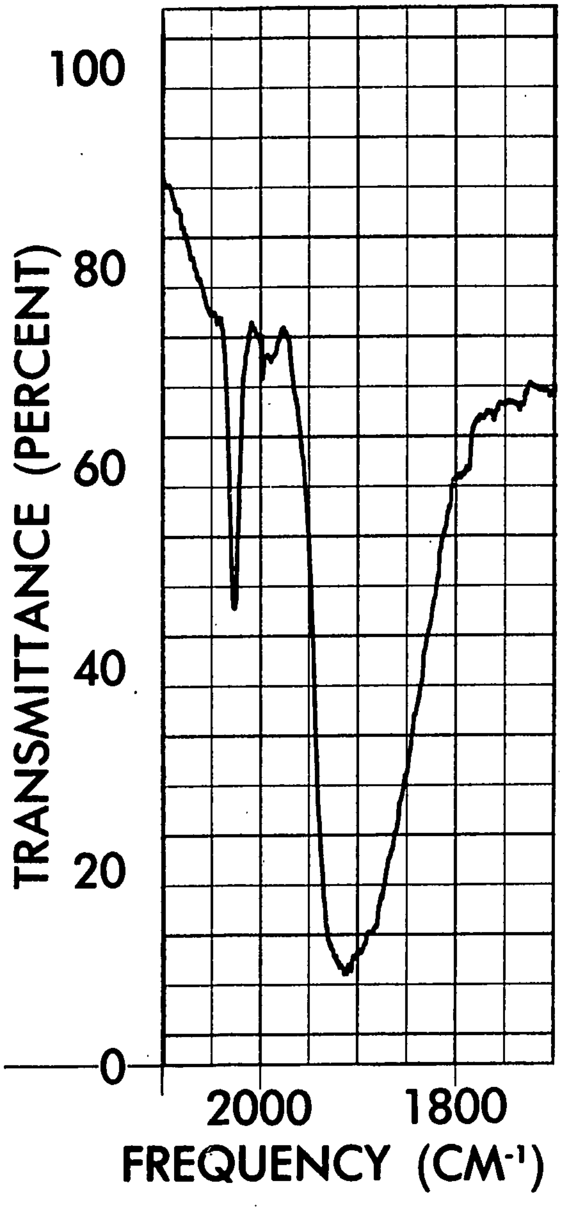
100
80
60
40
20
0
TRANSMITTANCE (PERCENT)
2000
1800
FREQUENCY (CM⁻¹)

Figure 8

reached within the time required to dissolve the iron carbonyl.

It is clear that the reaction does not go to completion. If a solution containing a large excess of methoxide over iron pentacarbonyl is diluted with methanol, the bands of $Fe(CO)_5$ appear and grow in intensity. The bands of the product fade and finally disappear as more methanol is added. Thus, the position of equilibrium is shifted by varying the mole ratio or concentration of reactants.

If the mole ratio of $Fe(CO)_5$ to OCH_3^- is increased to 1:14.5* a new band appears (figure 9). This broad band is centered at 1780 cm^{-1} and has a shoulder at about 1815 cm^{-1}. Undoubtedly this band is due to a new species, because as the 1780 cm^{-1} band becomes more intense with increasing methoxide concentration, the bands of the first product become less intense. That this second product is in equilibrium with the first was shown by diluting the solution with methanol. The band of the second product faded as the bands of the first product grew in. As

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*Hereafter, these solutions will be called simply 1:1, 1:7, or the 1:14.5 solutions, meaning the mole ratio of starting materials, $Fe(CO)_5$ to $NaOCH_3$.

Figure 9

Infrared spectrum of a 1:14.5 mole ratio of $Fe(CO)_5$ and $NaOCH_3$ in methanol

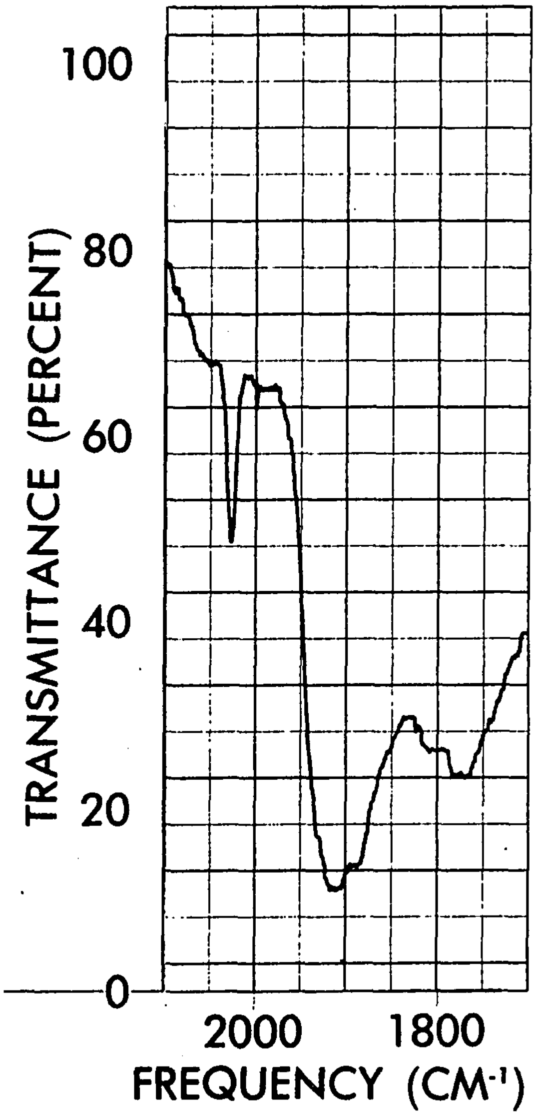
100
80
60
40
20
0
TRANSMITTANCE (PERCENT)
2000
1800
FREQUENCY (CM^{-1})

Figure 9

expected, addition of enough methanol drove the equilibrium back to a mixture of $Fe(CO)_5$ and the first product.

Some important information about the nature of the first product is immediately evident from these spectra. The product is not a loose association of iron pentacarbonyl and sodium methoxide, as stated by the earlier workers.[48,49] Such a loose adduct was supposed to consist of an essentially unmodified $Fe(CO)_5$ with the $NaOCH_3$ loosely coordinated in some manner. Since the $Fe(CO)_5$ moiety would retain D_{3h} symmetry it would be expected to give the same spectrum as unreacted $Fe(CO)_5$. This is clearly not the case. In fact there are now three bands and they appear at different frequencies from those of iron pentacarbonyl. Thus, there must be substantial modification of the iron carbonyl moiety. The information about the point group of the molecule that can be obtained from the carbonyl stretching bands will be considered in the Discussion.

The strongest band in the first product is about 100 cm^{-1} lower than the bands of $Fe(CO)_5$. This is very strong evidence that the product is an anion. The added negative charge is drained from the metal by greater back-bonding to the ligand. The increased participation of the π^*CO orbitals in bonding lowers the force constant of the

CO bonds and consequently the frequency of absorption. This, plus chemical evidence given below, will prove conclusively that the first product is an anion.

Infrared Spectra of Tetrahydrofuran Solutions

The first product can be prepared in tetrahydrofuran by the following procedure. Stock sodium methoxide solution is evaporated to dryness on a vacuum line. Tetrahydrofuran is distilled under vacuum onto the sodium methoxide. The methoxide is insoluble in THF but can be suspended fairly well by means of a magnetic stirrer. Iron pentacarbonyl is vacuum distilled into the THF suspension. The rate of reaction depends on how thoroughly the sodium methoxide is dispersed. If it is finely divided the reaction is complete within the minute or two required to mix the reactants.

A spectrum of a solution containing a 1:1 mole ratio of reactants (0.15 M) is shown in figure 10. Figure 11 is the spectrum of THF. The absence of the CO stretching bands of iron pentacarbonyl shows that the position of equilibrium is very close to completion in THF. Apparently the THF solubilizes the product to a greater extent than does methanol. The spectrum of the first product in THF is similar to that in methanol but with some

Figure 10

Infrared spectrum of the first
product in THF

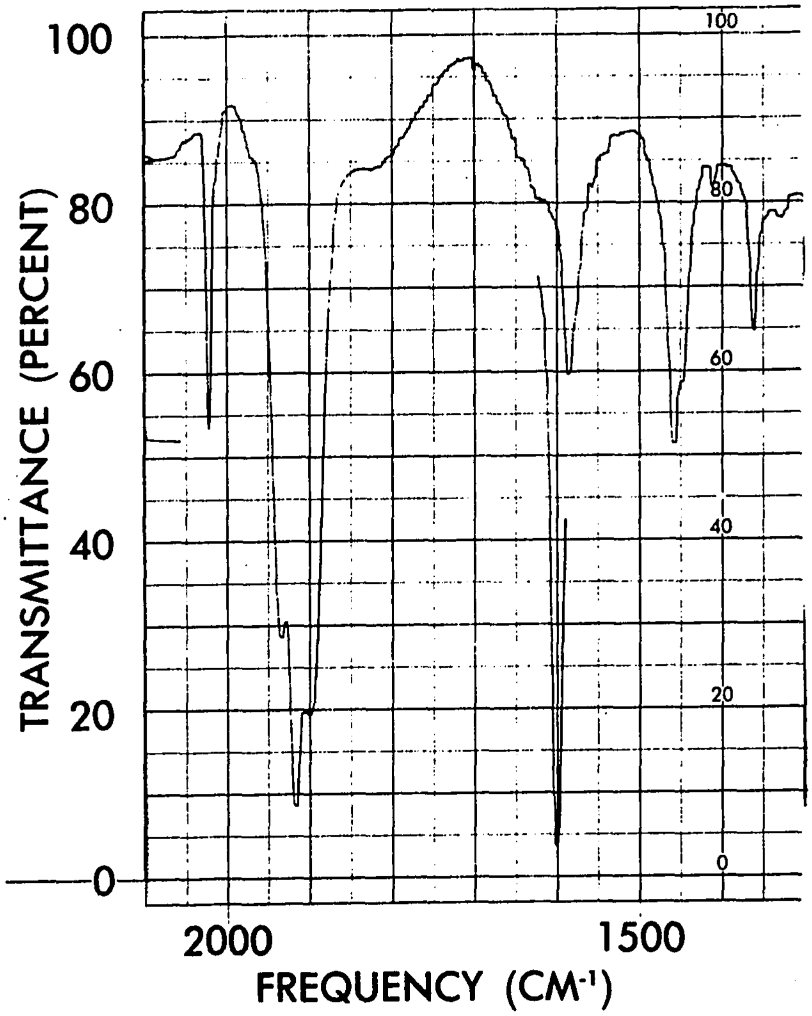
100
80
60
40
20
0
100
80
60
40
20
0
TRANSMITTANCE (PERCENT)
2000
1500
FREQUENCY (CM-1)

Figure 10

Figure 11

Infrared spectrum of THF

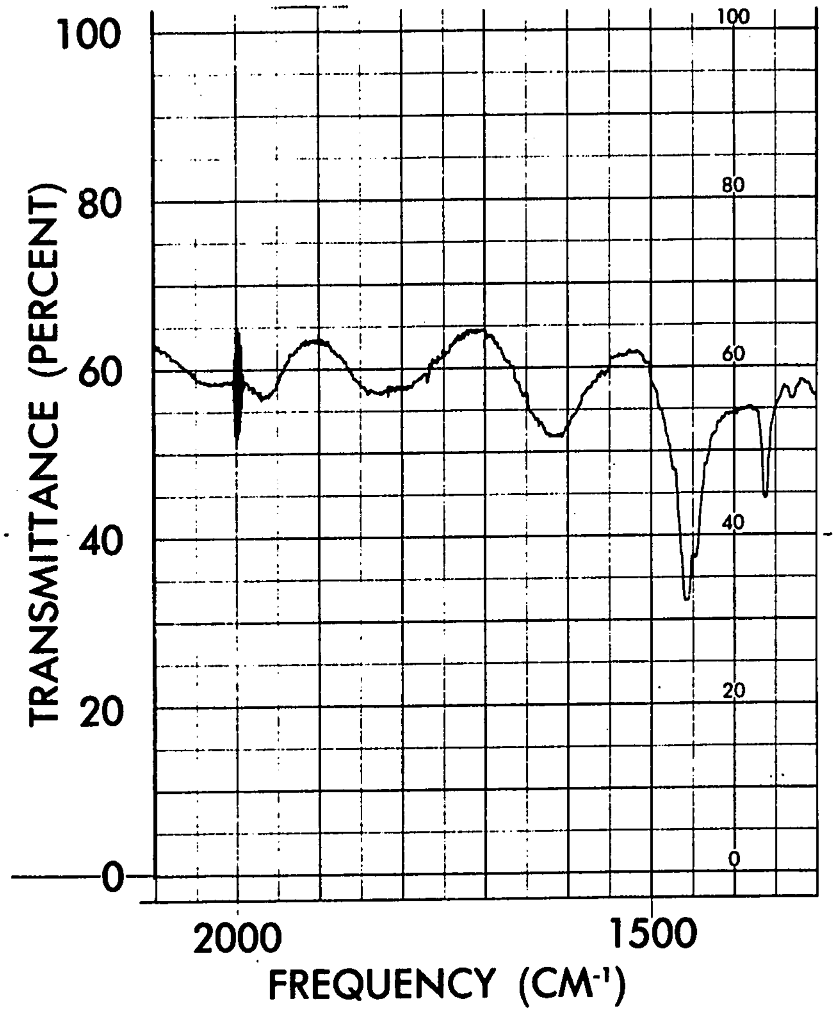
100
80
60
40
20
0
TRANSMITTANCE (PERCENT)
2000
1500
FREQUENCY (CM^{-1})

Figure 11

interesting differences. The sharp high frequency band has been shifted slightly to 2022 cm^{-1}. The lower frequency band is now resolved into three well-defined peaks, lying close together, at 1935 cm^{-1}, 1918 cm^{-1} and 1905 cm^{-1}. The location of these bands will be very useful for assigning the structure of the product. These spectra are summarized in table 1.

Another band in the THF spectrum bears heavily on the nature of the first product. This is the medium intensity band at 1586 cm^{-1}. This band can also be found in the methanol solutions if there is a large excess of methoxide, and the solution is concentrated. The band is located at 1590 cm^{-1} and is somewhat broader than in THF.

Finally, a weak band can be seen in the THF spectrum at 1413 cm^{-1}. The band is more clearly seen in figure 12, a spectrum of a more concentrated solution (1.5 M). In the spectra of methanol solutions this band is buried under the strong peak at 1450 cm^{-1} arising from methanol and the methoxide ion.

An attempt was made to prepare the second product in THF by the procedure followed for the first, except that a large excess of sodium methoxide was used (14.5 moles $NaOCH_3$ to 1 mole $Fe(CO)_5$). The mixture was stirred

TABLE 1

INFRARED C=O STRETCHING FREQUENCIES OF THE FIRST AND SECOND PRODUCTS

	Methanol Solutions	THF Solutions
First Product	2030 cm^{-1}	2022 cm^{-1}
	1910 cm^{-1}	1935 cm^{-1} 1918 cm^{-1}
	1885 cm^{-1}	1905 cm^{-1}
Second Product	1780 cm^{-1} 1815 cm^{-1} (sh)	--

Figure 12

Infrared spectrum of a concentrated solution of the first product in THF, showing the 1413 cm^{-1} band

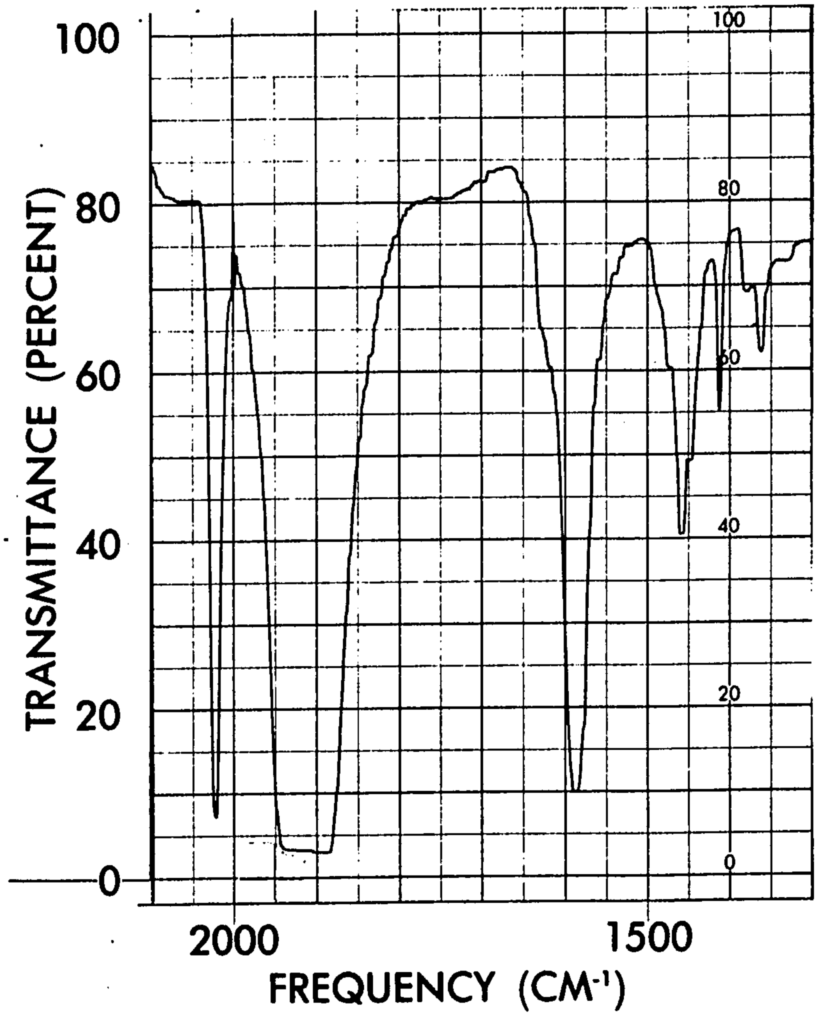
100
80
60
40
20
0
TRANSMITTANCE (PERCENT)
2000
1500
FREQUENCY (CM^{-1})
100
80
60
40
20
0

Figure 12

for 5 minutes. A large amount of the solid methoxide remained suspended at the end of this time. A spectrum of the supernatant liquid showed no bands other than the first product and THF. Stirring was continued for 45 minutes longer with no effect. Another reaction mixture was stirred in a 60°C water bath for half an hour but to no avail. The second product would not form in THF. The white solid remaining in the flask is sodium methoxide, as shown by the infrared spectrum of it in a Nujol mull.

Raman Spectra of Methanol Solutions

The usefulness of the infrared spectrum in discovering the point group of the products would be greatly enhanced by a knowledge of their Raman spectra. Unfortunately, this is one area where the moderate light sensitivity of the products was a serious handicap. Although the products were not appreciably affected by room light during their manipulation, the much more intense light of the laser exciting line caused decomposition as evidenced by a change in color of the solutions from pale yellow to deep orange. This difficulty was minimized as much as possible by using the exciting line farthest from the visible absorption of the compounds. The laser line closest in color to that of the solutions was chosen as the exciting light, namely the 632.8 nm line of a He-Ne laser. In addition it was necessary to employ low laser power (50 mw at the sample). This is a severe hindrance because Raman scattering is proportional to laser power. It was necessary to sacrifice signal to noise ratio in order to preserve the compound long enough to obtain its spectrum.

Sample containers for the Raman spectra were filled by syringe in a glove bag and temporarily sealed with a plug of clay. They were then removed from the glove bag one at a time, cooled in a dry ice-acetone bath and sealed off with a torch.

The Raman spectrum of the first product in methanol, shown in figure 13, was recorded directly on a chart. It has the same carbonyl stretching frequencies as the infrared spectrum: 2030 cm^{-1} (polarized), 1910 cm^{-1} (depolarized), and 1885 cm^{-1} (polarized). As can be seen from the spectrum a sloping polarized background was an additional problem.

Attempts to obtain the Raman spectrum of the second product failed due to the difficulties mentioned above. In addition the solutions could not be made more concentrated in metal carbonyl because increasing the concentration of iron pentacarbonyl drives the reaction

Figure 13

Raman spectrum of the first product
in methanol

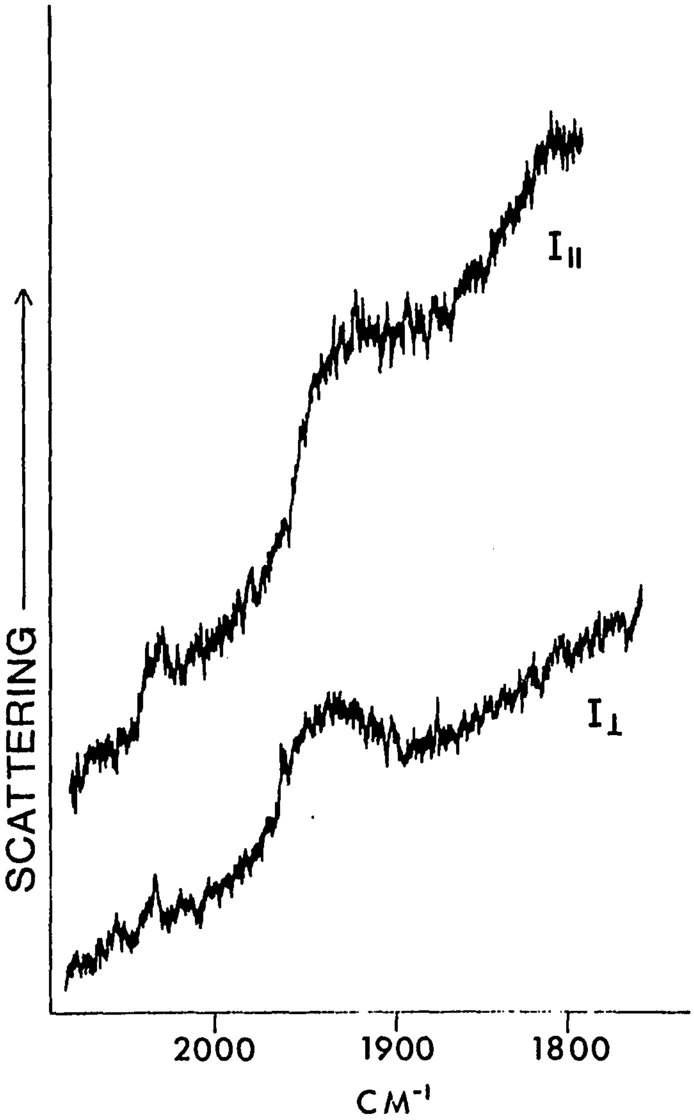

Figure 13

toward the first product, away from the second. The solutions could not be made more concentrated in sodium methoxide because they were already saturated.

Raman Spectra of Tetrahydrofuran Solutions

Tetrahydrofuran solutions of the first product are subject to the same light sensitivity problems as the methanol solutions. However, the better resolution of the bands in the THF infrared spectra was present in the Raman spectra as well. Unfortunately, as discussed above, the second product could not be prepared in THF. The THF spectra were recorded digitally on tape and plotted by a Complot digital plotter. Figure 14 is the Raman spectrum of a 1.5 M solution of the first product. The spectrum can be smoothed by means of a computer program* which calculates a moving average. The moving average is weighted by coefficients that result from a least squares fitting of some polynomial to the data.[55] The operator chooses the polynomial which gives the best smoothing without degrading the data. The smoothed spectrum is shown in figure 15. The THF and methanol solutions have the same

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*Thanks are due to Arthur Noguerola for the use of his program.

Figure 14

Raman spectrum of the first product
in THF (unsmoothed)

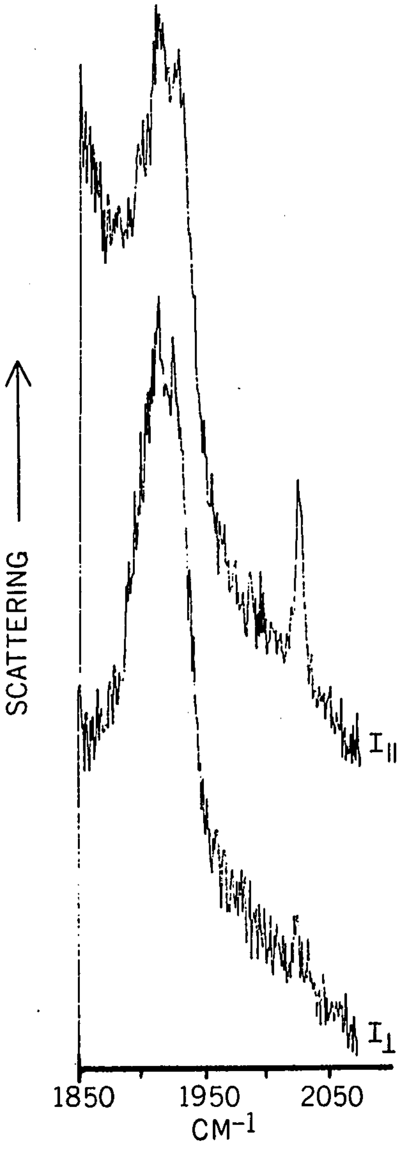


Figure 14

Figure 15

Raman spectrum of the first product
in THF (smoothed)

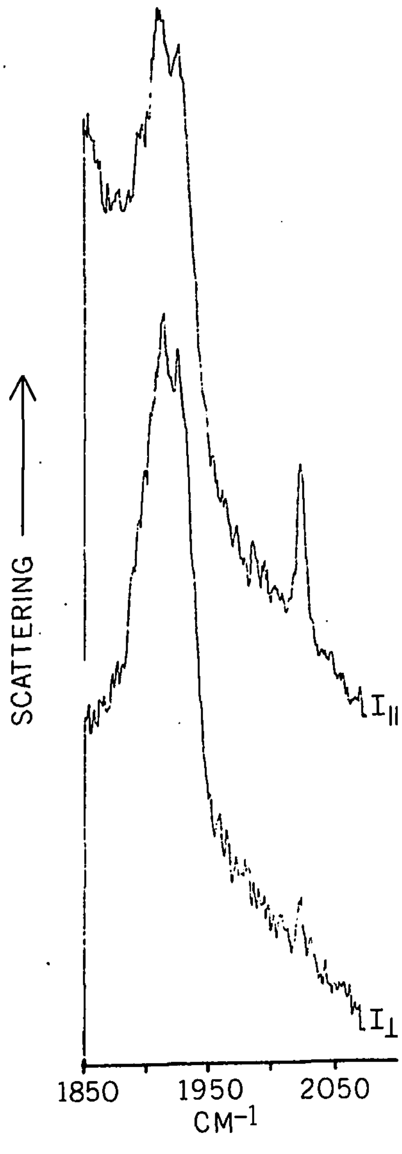


Figure 15

carbonyl stretching bands in the Raman as in the infrared spectra. In THF they are 2027 cm^{-1} (polarized), 1930 cm^{-1} (depolarized), 1917 cm^{-1} (depolarized), and a shoulder centered at 1905 cm^{-1} (polarized). The middle frequency region was searched for the 1586 cm^{-1} band, but no peaks were seen. Possibly this band is weak and is not observable due to the above-mentioned difficulties presented by these solutions. The Raman carbonyl stretching frequencies are summarized in table 2. The meaning of these spectra and further conclusions about the structure of the products will be given in the Discussion.

Proton Magnetic Resonance Spectra

Sample tubes for NMR spectra were sealed by a thin layer of silicone adhesive around the edge of the cap. This was deemed sufficient to prevent oxidation of the sample as there was no sign of decomposition after the spectra were taken. Hexamethyldisiloxane for internal standard was dried over 3A molecular sieves and deaerated. Spectra were taken with the variable temperature control set to 40°C. A 1:1 solution in THF (0.60 M) has a singlet 199 Hz downfield from HMS (figure 16). Spectra of methanol solutions have only the two methanol singlets. The location of these peaks for various methanol solutions is given in

TABLE 2

RAMAN C=O STRETCHING FREQUENCIES OF THE FIRST PRODUCT

Methanol Solutions		THF Solutions	
2030 cm^{-1}	polarized	2027 cm^{-1}	polarized
1910 cm^{-1}	depolarized	1930 cm^{-1} 1917 cm^{-1}	depolarized depolarized
1885 cm^{-1}	polarized	1905 cm^{-1}	polarized

Figure 16

^{1}H-NMR spectrum of the first product in THF. The two multiplets are due to THF. The singlet is due to the first product.

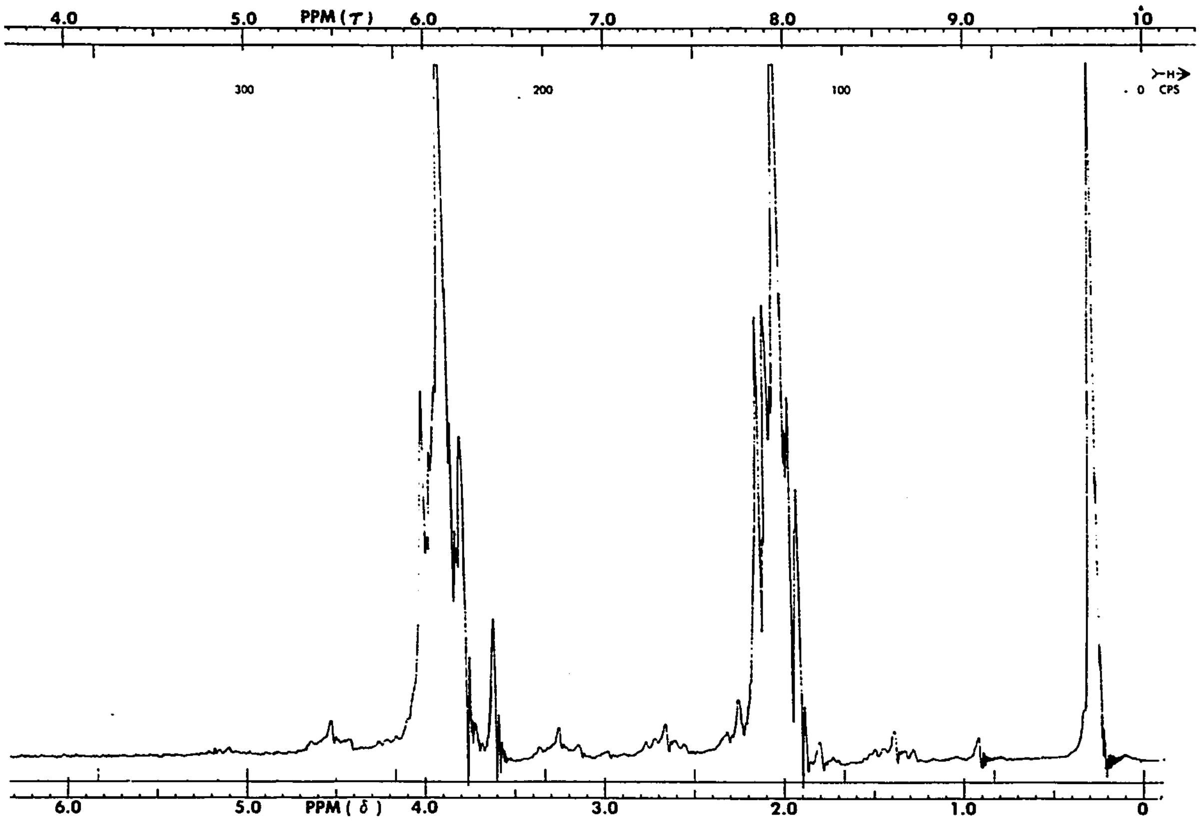


Figure 16

table 3. Clearly, there is rapid exchange among methanol, methoxide and the products. Further conclusions to be drawn from these spectra will be considered in the Discussion section.

Chemical Evidence

Are there any species present in the solutions other than the two products seen by infrared and Raman spectroscopy? To detect any other products that might be present the following experiments were performed.

A flask containing a methanol solution of the products was placed on a vacuum line. An emply flask fitted with a stopcock and ball joint adapter (figure 2) was connected to the line and cooled by a dry ice-trichloroethylene slush bath. The line was evacuated and closed off from the pump. Volatile material distilled under vacuum into the emply flask. With its stopcock closed the flask was removed from the line and capped with a socket joint and serum stopple. Samples for infrared spectra were withdrawn by syringe. The spectra showed only bands of methanol and iron pentacarbonyl. Hence, there are no reaction products more volatile than these. This experiment also points up the equilibrium nature of the reaction. Although there is not enough iron pentacarbonyl present at

TABLE 3

LOCATION OF PEAKS IN THE ^{1}H-NMR SPECTRA OF SOLUTIONS OF THE FIRST AND SECOND PRODUCTS IN Hz DOWNFIELD FROM HMS

	Methyl Protons	Hydroxyl Protons
Methanol Solutions		
CH_3OH	197	286
$NaOCH_3$ (2.1 M)	202	408
$NaOCH_3$ (4.3 M)	207	505
$(CO)_4FeCOOCH_3^-$ (0.3 M) and $NaOCH_3$ (1.7 M)	203	397
$(CO)_4FeCOOCH_3^-$ (0.1 M) and $(CO)_3Fe(COOCH_3)_2^{2-}$ (0.2 M) and $NaOCH_3$ (3.8 M)	207	488
THF Solution		
$(CO)_4FeCOOCH_3^-$	199	---

equilibrium in a 1:14.5 reaction to be observed in the infrared spectrum, much larger amounts can be collected in the cold trap. As some volatilizes the reverse reaction produces more.

No measurable amount of gas evolution was ever observed for any of the solutions.

Neutral metal carbonyls are soluble in hydrocarbons. To see if there were any neutral species present, metal carbonyl or otherwise, methanol solutions were extracted with hexane. Hexane (5.0 ml) was transferred by syringe to a centrifuge tube containing 5.0 ml of a 0.15 M methanol solution. The tube was shaken for a minute, the layers allowed to separate, and a sample of the hexane layer for an infrared spectrum was taken by syringe. The spectrum showed only hexane bands in the case of the 1:14.5 solution, and hexane and iron pentacarbonyl bands for the 1:1 solution. Spectra of the methanol layers taken after extraction retain all the product bands. These experiments confirm the assignment of the infrared bands to anionic first and second products. Since no other products were observed, some form of addition reaction between iron pentacarbonyl and methoxide ion is indicated.

Large anions are sometimes precipitated by large cations. It should be possible to obtain the first product as a precipitate by adding a suitable cation to the solution. The cesium ion (CsCl) was tried first, but it merely dissolved in the solution. The tetraphenylarsonium ion was found to work. Unfortunately, the large number of carbon and hydrogen atoms in this ion make elemental analysis relatively insensitive to changes of one or two carbon or hydrogen atoms in the formula of the precipitate.

A solution of the first product in methanol was prepared (1.5×10^{-3} mole $Fe(CO)_5$ to 1.5×10^{-3} mole OCH_3^- in a 1.2 M solution). Tetraphenylarsonium chloride (0.64 g, 1.5×10^{-3} mole) was dissolved in 2.0 ml methanol. This solution was added to the metal carbonyl solution by the double-ended needle technique (described above). A powdery yellow precipitate began to form within a few minutes. As the precipitation slowed the solid that came down was darker and more crystalline. After 15 minutes precipitation reached an apparent standstill. An infrared spectrum of the supernatant liquid (figure 17) showed only bands of methanol, except for a very weak 1910 cm^{-1} band. Thus, assignment of all the metal carbonyl bands in the 1:1 solution to an anionic first product is again confirmed.

The precipitate was collected on a Buchner funnel,

Figure 17

Infrared spectrum of supernatant liquid after precipitation of metal carbonyl anions with Ph_4As^+

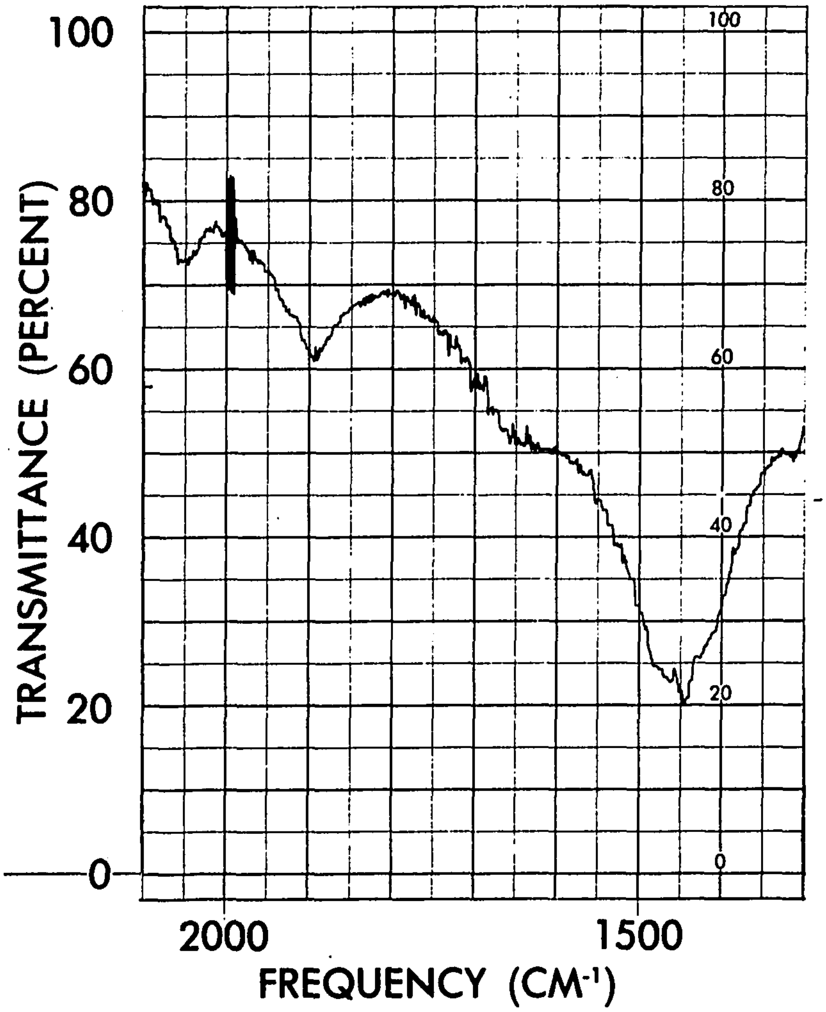

TRANSMITTANCE (PERCENT)
100
80
60
40
20
0
100
80
60
40
20
0
2000
1500
FREQUENCY (CM-1)

Figure 17

washed with a small amount of methanol and dried by suction. It was found that further attempts to purify the precipitate were more likely to decompose it. Elemental analysis by Galbraith Laboratories, Inc. gave the following results:

C 59.38 H 3.87 As 11.82 Fe 8.79

These percentages give a ratio of one atom of iron per one atom of arsenic. Since the tetraphenylarsonium ion has a charge of +1, the metal carbonyl anion must be mononegative. A less likely possibility is a dinegative metal carbonyl containing two iron atoms.

A spectrum of a Nujol mull of the precipitate is shown in figure 18. The CO stretching bands are shifted to lower frequencies but the basic pattern is the same as it was in the solution spectra. That there are no drastic changes in the carbonyl stretching region is good evidence that the metal carbonyl anion was only precipitated, but not altered in its composition.

Hydrolysis of the First Product

When small amounts of water are added to a 1:7 solution in methanol the infrared bands of the first product decrease in intensity with each addition and new bands grow in. When the amount of water reaches one mole of water per mole $Fe(CO)_5$ originally added, the bands of the first product are completely gone. Addition of more water has no

Figure 18

Infrared spectrum of the Ph_4As^+ salt of the first product (Nujol Mull)

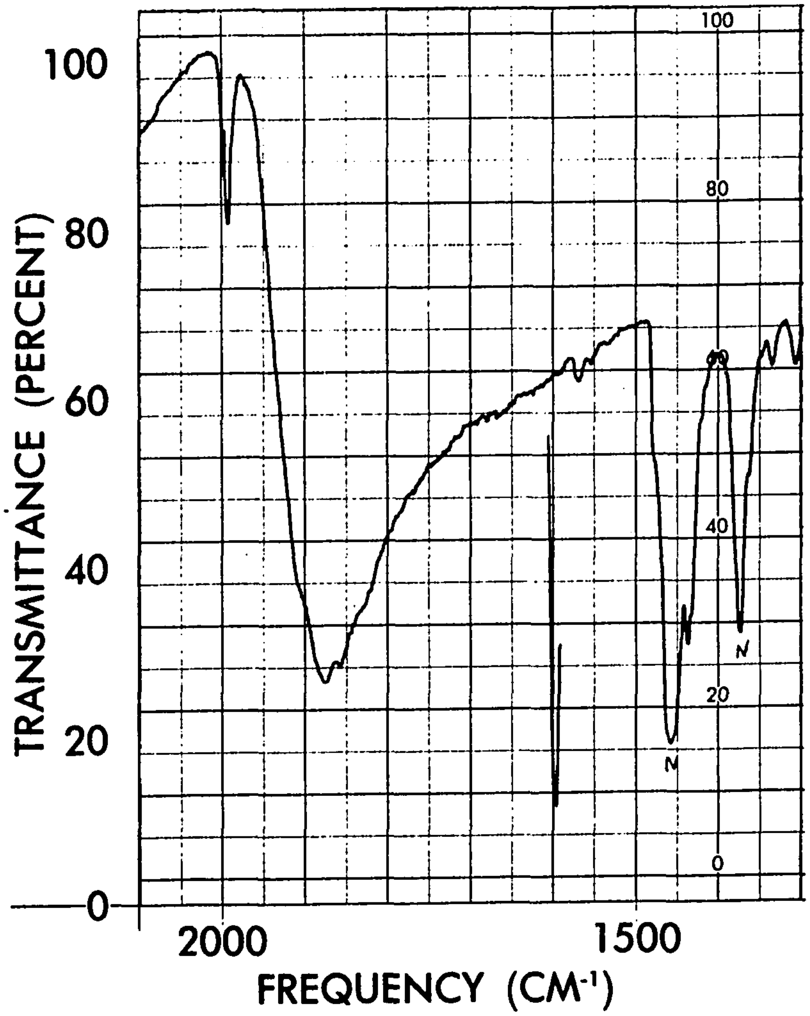

100
80
60
40
20
0
TRANSMITTANCE (PERCENT)
100
80
60
40
20
0
M
N
2000
1500
FREQUENCY (CM-1)

Figure 18

further effect on the spectrum except the broad 1640 cm^{-1} water band appears and grows in. The new metal carbonyl bands, figure 19, appear at 2008 cm^{-1} (medium, and 1890 cm^{-1} (strong) with a shoulder at 1918 cm^{-1} (strong-medium). Figure 20 is the spectrum of a partially hydrolyzed solution (1:3). A spectrum taken with cesium bromide windows shows the bands in the low wavenumber region, 700, 622, 599, 540 (very weak) and 480 cm^{-1} (figure 21). These low wavenumber bands are identical[56] with those in the spectrum of the known anion, hydridotetracarbonyl ferrate, $HFe(CO)_4^-$.

The carbonyl stretching bands of $HFe(CO)_4^-$ are somewhat solvent dependent.[57] In water they are 2015, 1933, and 1902 cm^{-1}, while in piperidine they are 1997, 1911, and 1883 cm^{-1}. In a solvent of intermediate polarity, such as methanol, one expects bands to be at frequencies between those of the above sets. Averaging the respective frequencies in water and piperidine one obtains 2006, 1922 and 1892 cm^{-1}. These values are very close to those actually obtained in methanol. The relative intensities of these bands match those of $HFe(CO)_4^-$ ie., medium, strong-medium, strong, reading from high wavenumbers to low. In addition to the above mentioned $HFe(CO)_4^-$ bands there are bands at

Figure 19

Infrared spectrum of the hydrolysis product, $HFe(CO)_4^-$, in methanol

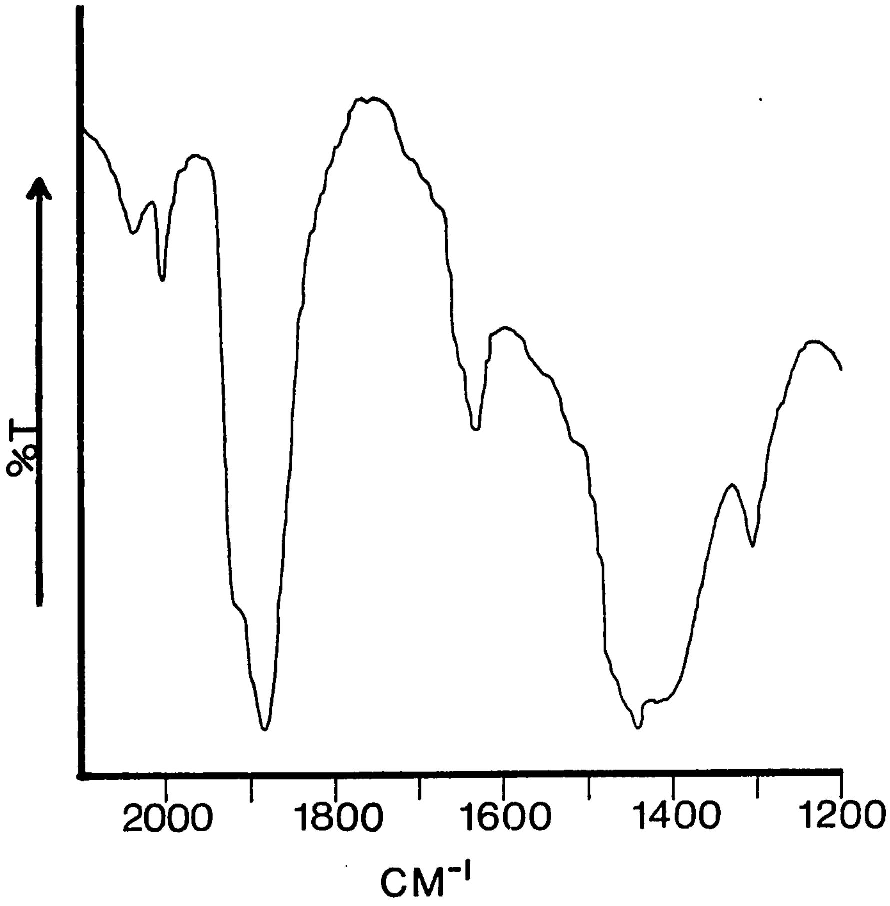


Figure 19

Figure 20

Infrared spectrum of a partially hydrolyzed methanol solution

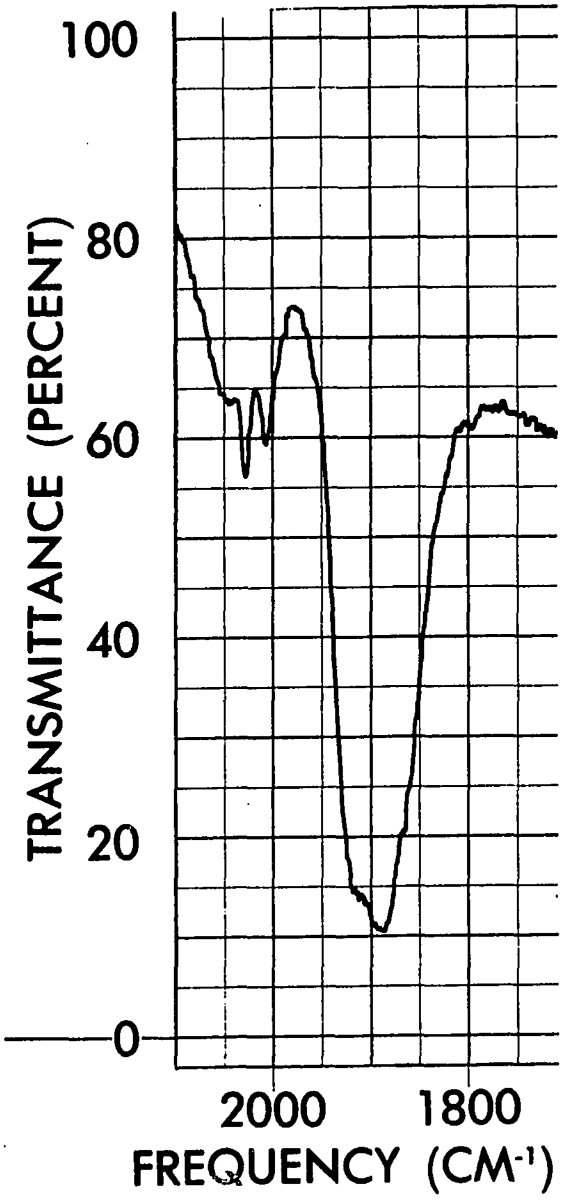

100
80
60
40
20
0
TRANSMITTANCE (PERCENT)
2000
1800
FREQUENCY (CM-1)

Figure 20

Figure 21

Infrared spectrum of $HFe(CO)_4^-$,
low wavenumber region

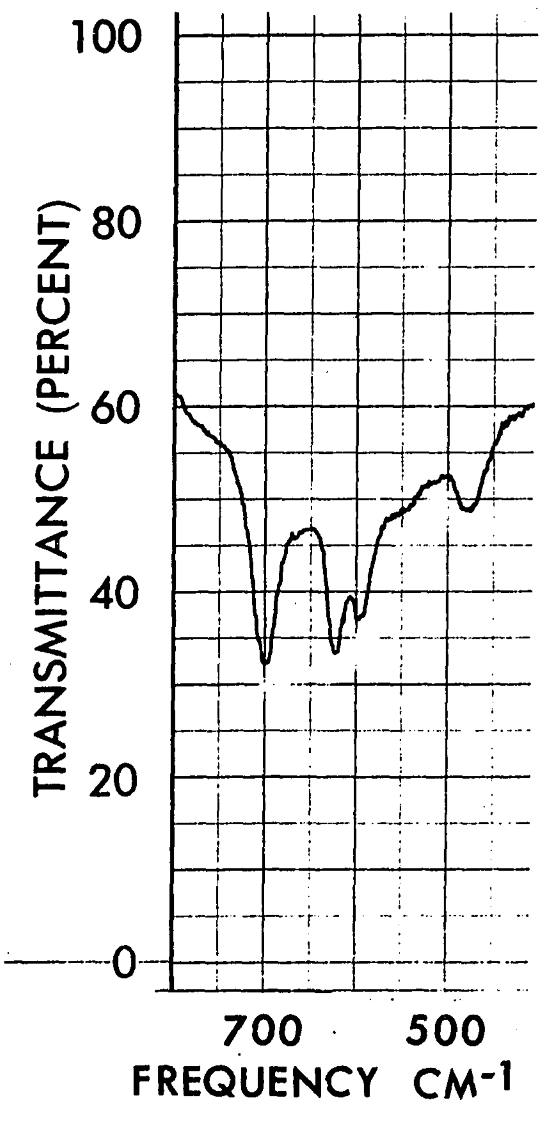

TRANSMITTANCE (PERCENT)
100
80
60
40
20
0
700
500
FREQUENCY CM-1

Figure 21

1640 cm^{-1} (medium, sharp) and 1310 cm^{-1}.

The above spectroscopic evidence for $HFe(CO)_4^-$ is complemented by chemical evidence. A solution of tetraphenylarsonium chloride in methanol was added to a completely hydrolyzed reaction mixture. At first a yellow powder formed slowly. With time the precipitate became more crystalline. After about 70 minutes most of the precipitate was crystalline. It was collected and dried. Elemental analysis was performed by Schwartzkopf Microanalytical Laboratory.

Calculated for $Ph_4As^+HFe(CO)_4^-$: C 60.90 H 3.83
As 13.57 Fe 10.11
Found: C 59.59 H 3.81
As 14.08 Fe 10.12

A spectrum of a Nujol mull of the precipitate was taken (figure 22). Again, the pattern of carbonyl stretching bands is the same as in methanol solutions, but the bands are shifted to lower frequencies. The 2008 cm^{-1} band is now at 1998 cm^{-1}. The 1890 cm^{-1} band and 1918 cm^{-1} shoulder have broadened into a single band centered at about 1860 cm^{-1}.

When the water is added to methanol solutions of the first product, crystals begin to form immediately. If all

Figure 22

Infrared spectrum of a Nujol Mull of $Ph_4As^+ HFe(CO)_4^-$

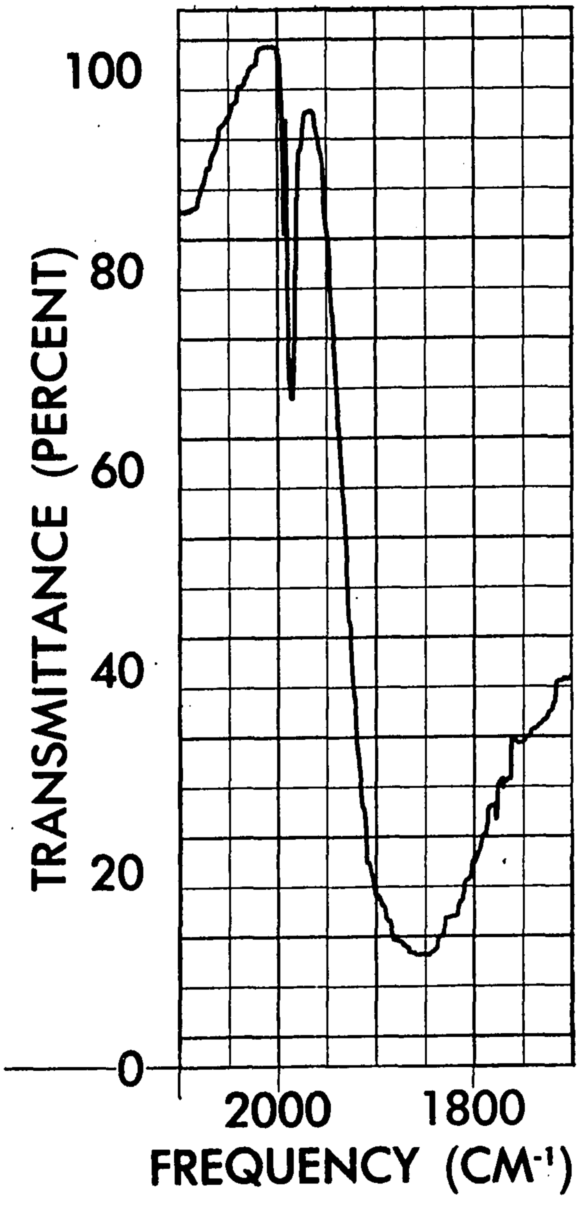

TRANSMITTANCE (PERCENT)
100
80
60
40
20
0
2000
1800
FREQUENCY (CM-1)

Figure 22

the product is hydrolyzed, the white needles form quickly. Elemental analysis by Schwartzkopf Microanalytical Laboratory identified it as sodium methylcarbonate.

Calculated for $NaOC(=O)OCH_3$:	C	24.50	H	3.80	Na	23.45
Found:	C	24.12	H	3.17	Na	22.32

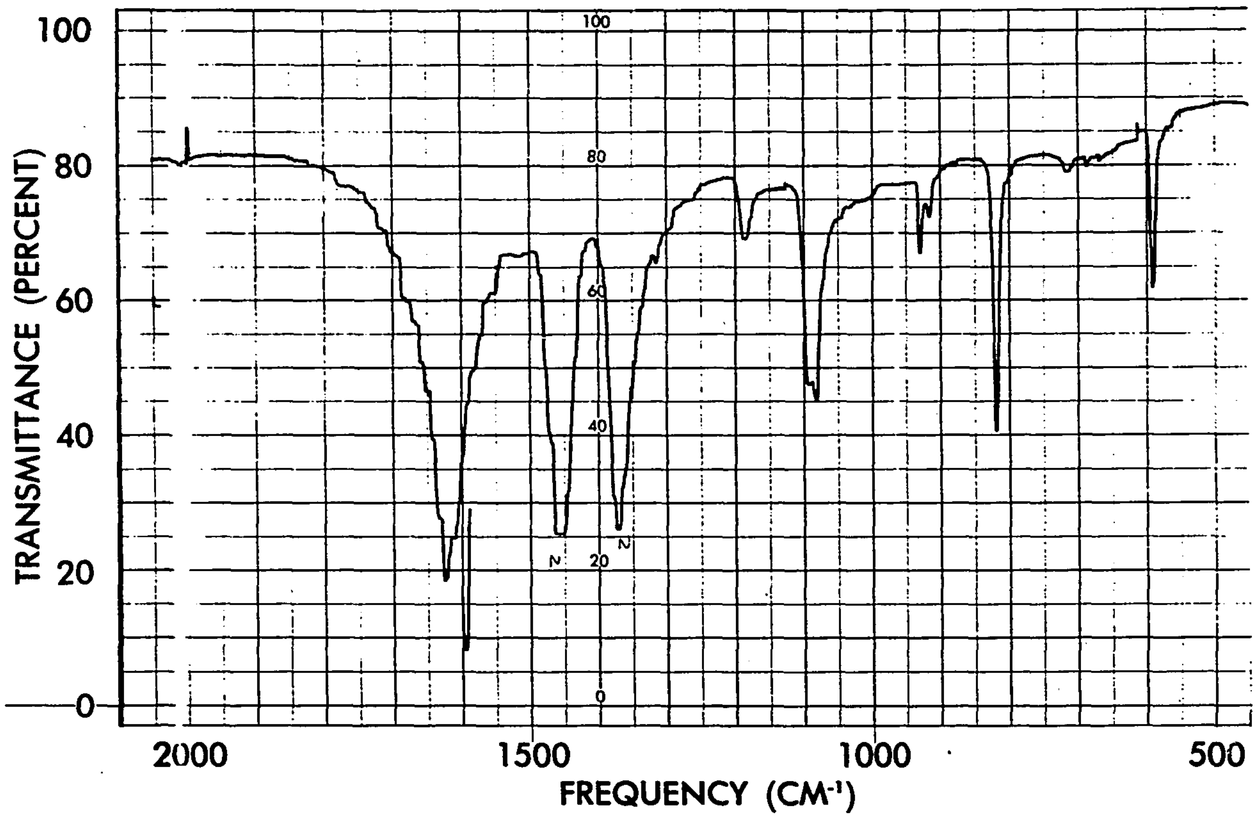
The infrared spectrum of the precipitate (KBr and Nujol mull) was compared to spectra of various sodium salts of carbon and oxygen containing acids: sodium carbonate, sodium hydrogen carbonate, sodium acetate, sodium formate, and sodium methylcarbonate. The spectrum of sodium methylcarbonate was identical to that of the crystals; the other spectra were quite different.

Sodium methylcarbonate was dissolved in methanol. The infrared spectrum of this solution has bands at 1640 cm^{-1} (medium, sharp) and 1310 cm^{-1}. This completes the assignment of all the bands in the spectrum of hydrolysis products. Figures 23 and 24 are spectra $NaOC(=O)OCH_3^-$ as a Nujol mull and in methanol respectively.

A conclusion can be drawn from the formation of sodium methylcarbonate in the hydrolysis reaction. The presence of this product implies that the $HFe(CO)_4^-$ could not have been produced by reaction of unreacted $Fe(CO)_5$

Figure 23

Infrared spectrum of a Nujol Mull of
sodium monomethylcarbonate



TRANSMITTANCE (PERCENT)
100
80
60
40
20
0
2000
1500
1000
500
FREQUENCY (CM⁻¹)

Figure 23

Figure 24

Infrared spectrum of a methanol solution
of sodium monomethylcarbonate

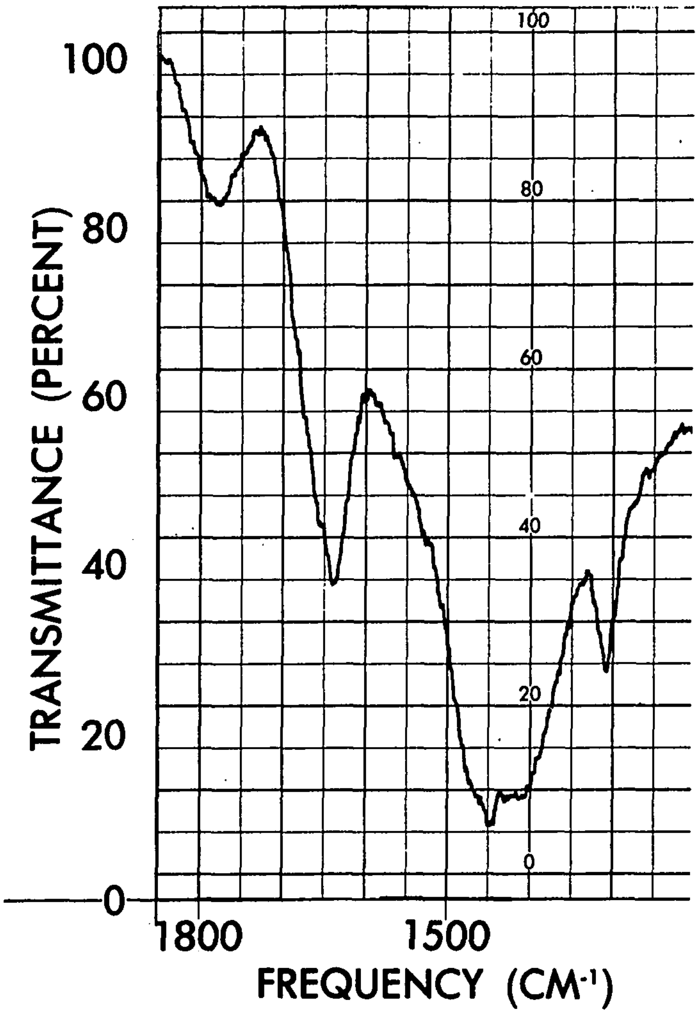

100
80
60
40
20
0
TRANSMITTANCE (PERCENT)
1800
1500
FREQUENCY (CM^{-1})

Figure 24

with OH^- (possibly formed from H_2O and unreacted OCH_3^-). This reaction is known to produce sodium carbonate.[33]

$$Fe(CO)_5 + 3OH^- \longrightarrow HFe(CO)_4^- + H_2O + CO_3^{2-} \qquad (58)$$

However, no sodium carbonate was found in the hydrolyzed solutions, only sodium methylcarbonate.

If a solution of lower mole ratio, which contains considerable amounts of iron pentacarbonyl, is hydrolyzed, the bands of $Fe(CO)_5$ decrease in intensity along with the bands of the product. As the product is used up in the hydrolysis, the reactants, $Fe(CO)_5$ and OCH_3^-, produce more. In this manner, all of the $Fe(CO)_5$ is converted to product and then hydrolyzed.

What is known so far about the hydrolysis of the first product is summarized in the equations below:

$$Fe(CO)_5 + OCH_3^- \rightleftharpoons \text{product} \qquad (59)$$

$$\text{product} + H_2O \longrightarrow HFe(CO)_4^- + OC(=O)OCH_3^- \qquad (60)$$

These equations would be much more useful in discovering the nature of the product if they included the stoichiometry. Since the reaction of iron pentacarbonyl with sodium methoxide in methanol does not go to completion, it is not possible to obtain the stoichiometry by a Job/Yoe plot.

This is clearly illustrated in figure 25, a plot of the absorbance of the 2020 cm^{-1} band of $Fe(CO)_5$ versus the mole ratio of $Fe(CO)_5$ to OCH_3^-. Each addition of methoxide pushed the equilibrium further toward products, using up more $Fe(CO)_5$. The plot is a smooth curve; no cut off point is obtained.

The hydrolysis, however, does go to completion, as evidenced by the infrared spectra. A series of reactions was done using a constant amount of iron pentacarbonyl with varying amounts of sodium methoxide. Enough water was present to hydrolyze all the product. The absorbance of the 1890 cm^{-1} band was plotted against the mole ratio of $Fe(CO)_5$ to OCH_3^-. As can be seen in figure 26, the absorbance (and, therefore, the concentration of $HFe(CO)_4^-$) rose quickly to a maximum at 1:2 and then declined. Hence, the overall stoichiometry of reaction plus hydrolysis is one mole of iron pentacarbonyl per two moles of methoxide ion.

Ordinarily, the concentration of $HFe(CO)_4^-$ would be expected to remain constant after the stoichiometric ratio of reactants had been reached. Yet, in this case, the amount declined. The reason for this is that the extra, unreacted OCH_3^- now combined with the $HFe(CO)_4^-$.

Figure 25

Job/Yoe plot of the first product
The absorbance of the 2020 cm^{-1} band of $Fe(CO)_5$ is plotted vs. the mole ratio of $Fe(CO)_5$ to OCH_3^-.

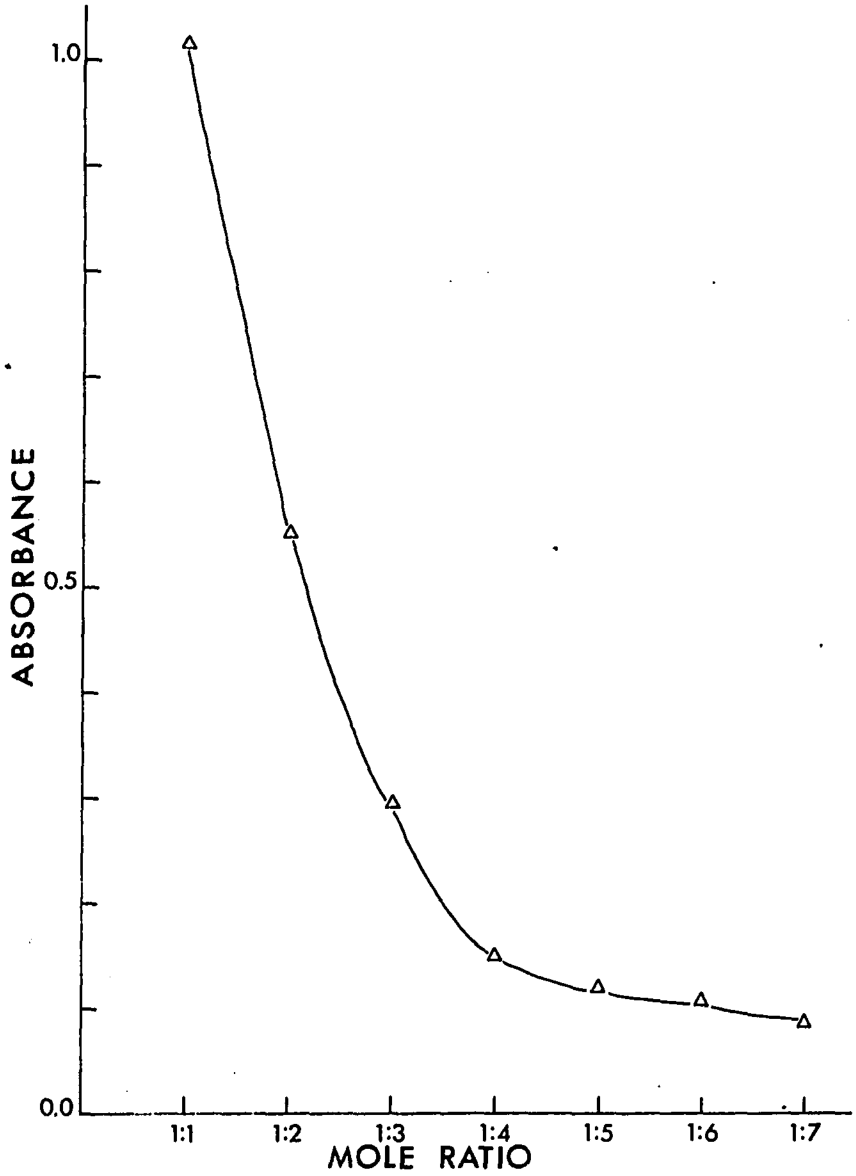


Figure 25

Figure 26

Job/Yoe plot of the hydrolysis product, $HFe(CO)_4^-$. The absorbance of the 1890 cm^{-1} band of $HFe(CO)_4^-$ is plotted vs. the mole ratio of $Fe(CO)_5$ to OCH_3^-.

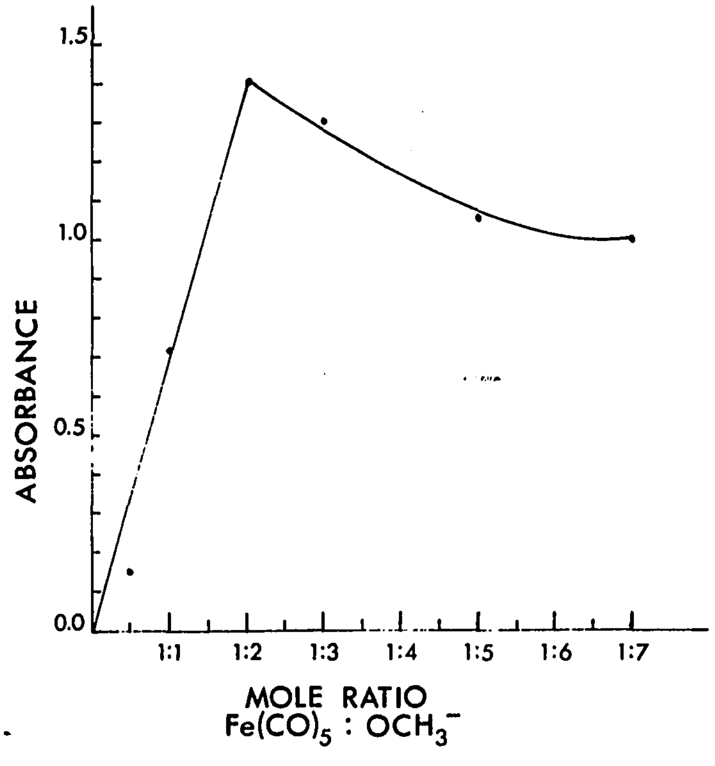

ABSORBANCE
1.5
1.0
0.5
0.0
1:1
1:2
1:3
1:4
1:5
1:6
1:7
MOLE RATIO
Fe(CO)5 : OCH3−

Figure 26

$$HFe(CO)_4^- + OCH_3^- \rightleftharpoons Fe(CO)_4^{2-} + HOCH_3 \qquad (61)$$

This is analogous to the acid--base equilibrium known[34] for $HFe(CO)_4^-$ and hydroxide, $K \approx 4 \times 10^{-14}$.

$$HFe(CO)_4^- + OH^- \rightleftharpoons Fe(CO)_4^{2-} + H_2O \qquad (62)$$

The Job/Yoe plot declined in a smooth curve, as expected for reactions that do not go to completion.

Hydrolysis of the First and Second Products

The hydrolysis of solutions containing the first and second products differs in a few aspects from hydrolysis of solutions containing only the first product. These differences are due mainly to the presence of the larger excess of methoxide required for the formation of the second product. The high concentration of OCH_3^- makes the $OCH_3^- + H_2O$ reaction more competetive with the others. The reaction of the OCH_3^- can be traced in a rather insensitive manner through successive additions of water by the characteristic shape of the 1450 cm^{-1} C--H deformation band. (Compare the spectra of methanol and sodium methoxide in methanol, figures 5 and 6 respectively.) Because some of the water is taken up by OCH_3^-, addition of amounts of water sufficient to cause complete hydrolysis of a 1:1

solution resulted in only partial hydrolysis of a 1:14.5 solution. As more and more water was added, the bands of the first product slowly gave way to bands of $HFe(CO)_4^-$. Eventually the broad 1640 cm^{-1} water bending band appeared. The white precipitate that formed with each addition of water was sodium methylcarbonate. After addition of a large excess of water it was hydrolyzed by the OH^- that had formed. The 1780 cm^{-1} band became more intense and lost its shoulder. The meaning of this will be understood after more evidence is given concerning the second product.

Hydrolysis of THF Solutions

Hydrolysis can be carried out on THF solutions of the product, and same hydrolysis products are obtained. The white precipitate was shown to be sodium methylcarbonate by its spectrum in a Nujol mull. The spectrum of the supernatant liquid (figure 27) has the bands of $HFe(CO)_4^-$ and $Fe(CO)_5$. The $HFe(CO)_4^-$ bands are shifted to lower frequencies in THF and occur at 1910 cm^{-1} and 1880 cm^{-1}. The Discussion section will deal with the route of formation of $Fe(CO)_5$ in this hydrolysis.

Concerning the Stability of the Products

The high reactivity of the first and second products has been stressed in the section concerned with precautions

Figure 27

Infrared spectrum of hydrolysis products of a solution of the first product in THF

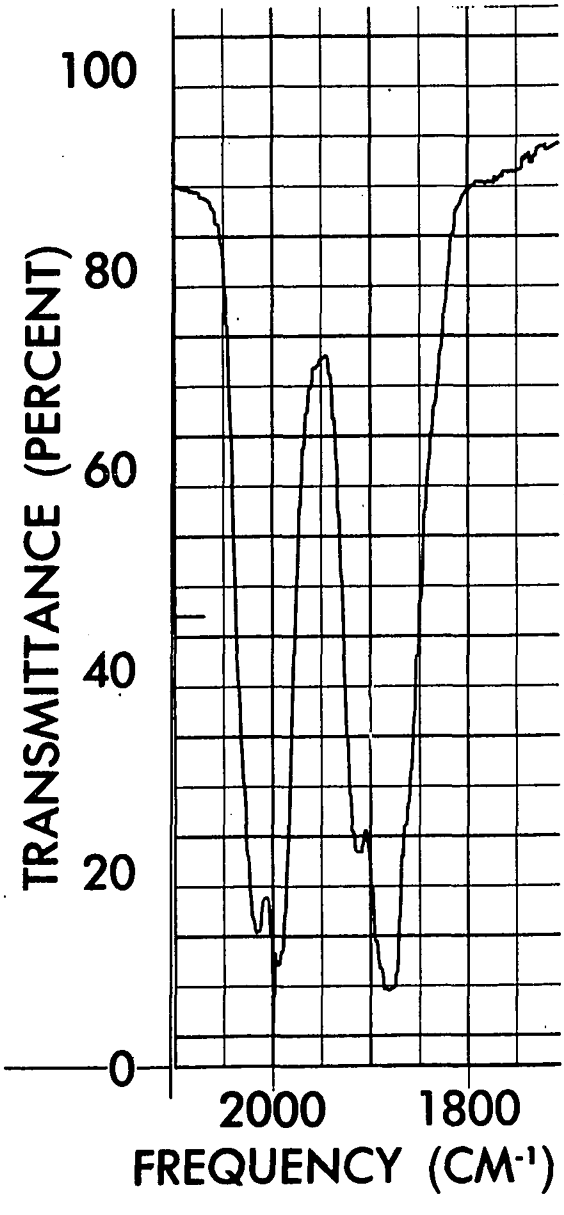

100
80
60
40
20
0
TRANSMITTANCE (PERCENT)
2000
1800
FREQUENCY (CM-1)

Figure 27

against water, oxygen and light. However, although reactive, the products are quite stable. Solutions have been kept for several months with no change in their appearance or their infrared spectra.

It sometimes happened that after several samplings a solution turned orange, then red. When dry oxygen was bubbled through a methanol solution of the products, the solution changed color immediately. A few seconds of gentle bubbling turned the solution from yellow to orange to red. There was no detectable change in the infrared spectrum. Evidently, the red species being formed has a very high extinction coefficient and trace amounts not visible in the infrared spectrum are sufficient to color the solution red.

With larger amounts of oxygen (about 10 minutes of bubbling) a brown solid formed and the solution turned opaque brown. Figure 28 is the infrared spectrum of an oxidized 1:14.5 solution. The bands of the product are gone and new bands occur at 1940 cm^{-1}, 1885 cm^{-1} and 1865 cm^{-1}. The latter two are a broad doublet. Two broad weak bands can be distinguished at 1615 cm^{-1} and 1665 cm^{-1}. This spectrum is identical to that of solutions which have changed color over a period of time. Therefore, accidental oxidation of such solutions was occuring.

Figure 28

The effect of oxygen on the infrared spectrum of a methanol solution of the products

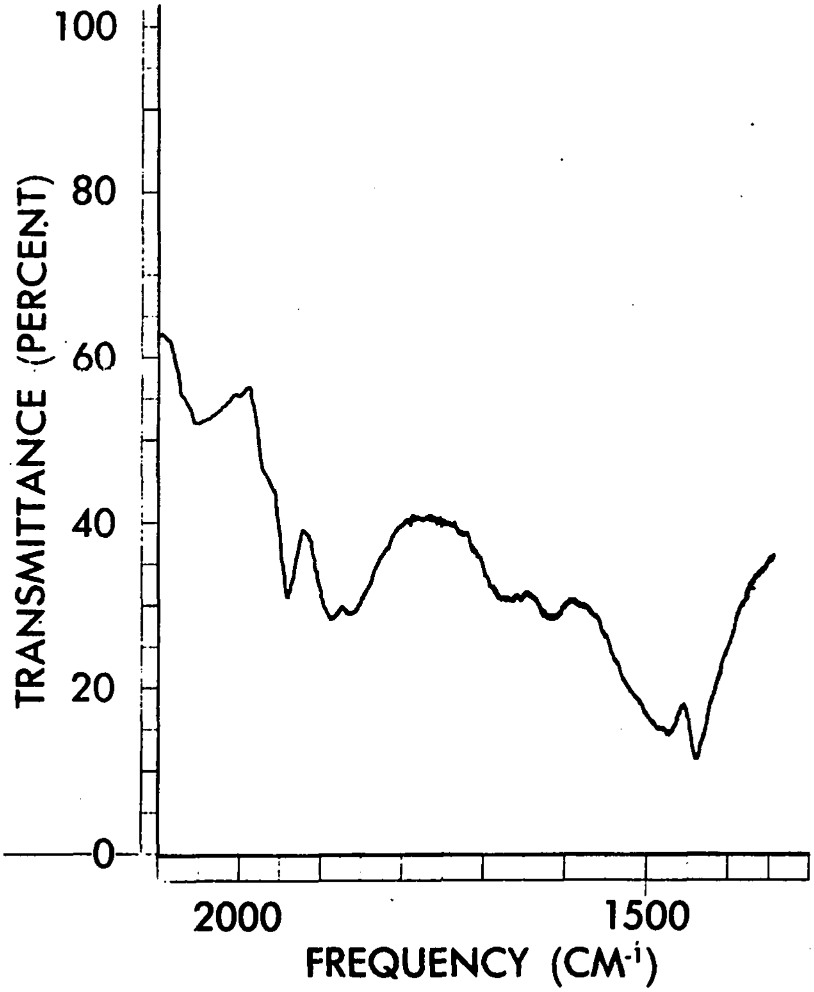

100
80
60
40
20
0
TRANSMITTANCE (PERCENT)
2000
1500
FREQUENCY (CM⁻¹)

Figure 28

Dilute solutions of $HFe(CO)_4^-$ are yellow. This anion reacts with oxygen to give the polynuclear metal carbonyl species, $Fe(CO)_8^{2-}$ and $Fe(CO)_{12}^{2-}$, which are red.[33] Oxidation of the products probably results in red polynuclear species similar to these.

Oxidation takes a different course in THF solutions. Bubbling in oxygen results in a decrease in intensity of the bands of the first product, and the appearance and then growth of $Fe(CO)_5$ bands. The yellow solution does not change color. Apparently, the oxidation product formed in methanol, which is probably a polynuclear anion, is not sufficiently solubilized by THF to form in these solutions.

DISCUSSION

A large body of evidence has been gathered concerning the first and second products. Some conclusions have already been drawn from this evidence. This section will show how the results lead to an elucidation of the structure of the products.

The section begins with a summary of preliminary results. This is followed by a detailed discussion of the infrared and Raman spectra of the first product, in which the symmetry of the product is determined. These spectra, plus NMR and chemical evidence, are used to complete the identification of the product. A reaction scheme is given which includes the formation of the product and its hydrolysis.

The discussion then turns to the second product, which is identified by infrared and chemical evidence. Some further properties of the products are given. The section closes with a consideration of the iron pentacarbonyl-methoxide reaction and the carbonyl insertion mechanism.

Preliminary Results

To begin with, the first product is not the loose adduct proposed in the literature.[48,49] This has been demonstrated in many ways by the experiments. Most convincing is the large difference between the carbonyl stretching regions in the infrared spectrum of iron pentacarbonyl and of the product. This can result only from substantial modification of the $Fe(CO)_5$ moiety.

It was also seen that the product is an anion. Metal carbonyl anions have carbonyl stretching frequencies that are substantially lower than those of neutral species. This results from increased backbonding to the CO ligand, which shifts negative charge from the metal to the ligand. The backbonding is accomplished by increased participation of the π^*CO molecular orbital in bonding. The additional negative charge raises the energy of the metal 3d orbitals resulting in more efficient overlap with the π^*CO molecular orbitals. As the contribution of antibonding orbitals increases, the bond order, and hence the force constant, of the CO bonds decreases. Since the force constant is lowered, the stretching frequency must decrease. In the case of the product the decrease is from approximately 2000 cm^{-1} for the neutral species, iron pentacarbonyl, to 1910 cm^{-1} for the strongest band of the anion.

The product formed a precipitate with the Ph_4As^+ cation. This would not occur for a neutral or cationic product. As has been mentioned in the Experimental, elemental analysis gave one iron atom per arsenic atom in the precipitate. Therefore, since the tetraphenylarsonium ion is monopositive the product must be mononegative.

Finally, it is clear that the reaction does not go to completion. The bands of iron pentacarbonyl are present in the infrared spectrum of the solutions unless they contain a large excess of methoxide ion. The position of equilibrium was shifted readily by varying the mole ratio or concentration of reactants. Moreover, when vacuum distillation or extraction with non-polar solvents removed iron pentacarbonyl from the solutions, the system restored the disturbed equilibrium by producing more.

No precipitation or gas evolution was observed for any of the solutions of the products. Neither did the extraction or vacuum distillations reveal the presence of any other products. A single anionic product has been formed, which implies that the reaction is some sort of simple addition of $Fe(CO)_5$ and OCH_3^-.

Identification of the First Product

Infrared and Raman spectra of solutions of the first product are identical in the carbonyl stretching region. In methanol the pattern of bands from high frequency to low is the following:

FREQUENCY	INTENSITY	ρ
2030 cm^{-1}	medium	polarized
1919 cm^{-1}	strong	depolarized
1885 cm^{-1}	strong-medium	polarized

Figure 29 lists the possible monosubstituted structures for the product, and the infrared and Raman CO stretching modes expected for each. Of the three, only one is expected to have three bands in both the infrared and Raman spectra. It is the axially substituted trigonal bipyramid.

The depolarization ratios of the bands are consistent with this structure. Polarized Raman bands arise from totally symmetric modes (A_1), while depolarized bands are due to all others. For the axially substituted structure, modes of symmetries $2A_1 + E$ are predicated: two polarized bands and one depolarized band are seen in the spectra.

Compounds of this structure have been found experimentally[42] to have the pattern in the infrared CO stretching

Figure 29

Possible monosubstituted structures for the first product, and the infrared and Raman active C=O stretching modes expected for each

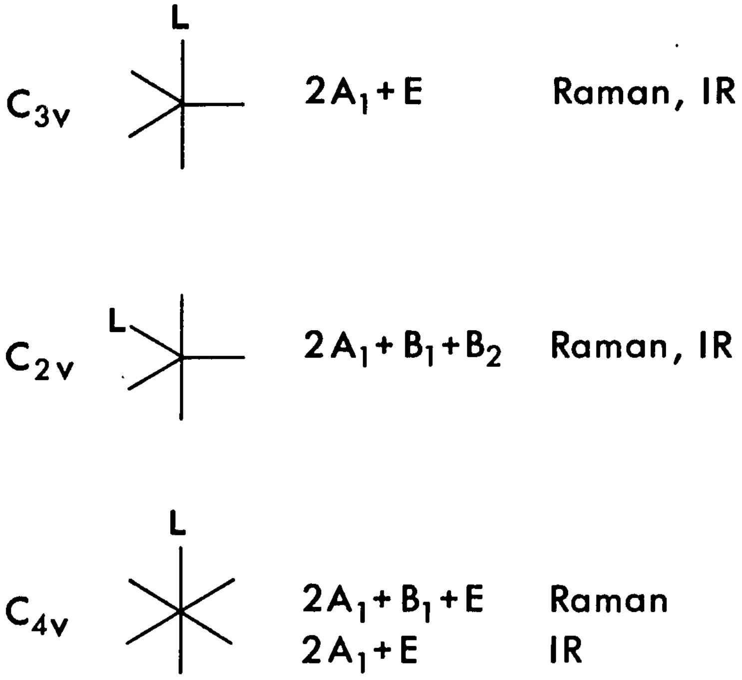

L
C_{3v}
$2A_1+E$
Raman, IR
L
C_{2v}
$2A_1+B_1+B_2$
Raman, IR
L
C_{4v}
$2A_1+B_1+E$
Raman
$2A_1+E$
IR

Figure 29

region:

weak-medium	A_1
medium	A_1
strong	E

The corresponding bands of the product have the same relative intensities. Although A_1 modes usually give rise to the strongest bands in the Raman spectra, the totally symmetric C=O stretching bands of metal carbonyls are frequently weak.[58] This is true of the product as well, which has medium intensity A_1 bands.

However, the product spectrum has an A_1 mode as the lowest frequency band instead of the E mode, but this can be understood. For complexes of the type axial $LFe(CO)_4$, the high frequency A_1 mode has been assigned to symmetric stretch of the equatorial CO's, and the low frequency A_1 to the axial CO stretch.[59] (The E mode is the equatorial asymmetric stretch.) The force constant of a carbonyl group is lowered when it is trans to some other, non-acceptor ligand. If this ligand bears a negative charge it is reasonable to expect further lowering of the force constant because some of the negative charge would be donated to the trans CO through the metal d and p orbitals they share. Since the E and the axial A_1 modes are fairly close in frequency, as seen in $HFe(CO)_4^-$ for example, it is not unreasonable to say that in this case the frequency of the A_1 mode has been decreased enough to make it the lowest frequency band.

The CO stretching bands of the THF solutions are similar in appearance to the bands of the methanol solutions.

The differences are due to a change in the solvent-solute interactions when the solvent is changed. Band broadening and small frequency shifts have been observed in the spectra of metal carbonyls as the polarity of the solvent increases.[60]

The half-band widths of the 1590 cm^{-1} and 2030 cm^{-1} bands in methanol are greater than those of the corresponding bands in THF.* Often the lower frequency bands are more solvent sensitive, and in this case, too, the 1590 cm^{-1} band experiences greater broadening.[61]

The solvent shifts of the product CO stretching bands are consistent with shifts given in the literature for a variety of complexes, ie., the shift is to lower frequency in the more polar solvent.[60,61]

---

*The dielectric constants of methanol and THF are 32.6 and 7.32 respectively.

THF	METHANOL
2022 cm^{-1}	2030 cm^{-1}
1935 and 1918 cm^{-1}	1910 cm^{-1}
1905 cm^{-1}	1885 cm^{-1}

The highest frequency band does not conform to the generalization, however, The same behavior is reported for the A_1 CO stretching band of $Co(CO)_3NO$, and is due to mixing of the CO stretching modes.[60,62] This observation is in line with the assignment of the highest frequency band to the symmetric equatorial stretching mode. Indeed, this mode must be mixed with axial CO stretching or it would not be infrared active.

The most striking solvent effect is the appearance of four bands in the 2000 cm^{-1} region of THF solutions as opposed to three for the methanol solutions. In spectra of methanol solutions the band at 1910 cm^{-1} and shoulder at 1885 cm^{-1} are rather broad. The corresponding bands for the THF solutions are sharper and the new band appears among them. This can be explained as a lifting of the degeneracy of the E mode.

The deduction of three modes, $2A_1 + E$, for the axially substituted trigonal bipyramid assumed perfect C_{3v}

symmetry. A sufficiently asymmetric ligand causes a perturbation of the idealized structure. This results in a broadening of the band for the methanol solutions, and complete splitting into a doublet in THF (1935 and 1918 cm^{-1}). The bands do not appear to be of equal intensity because of overlapping with the 1905 cm^{-1} band.

As anticipated, the depolarization ratios of the Raman bands of the THF solutions support this assignment. The bands attributed to the E mode are depolarized.

2027 cm^{-1}	polarized	equatorial symmetric stretch	A_1
1930 cm^{-1}	depolarized	equatorial asymmetric stretch	E
1917 cm^{-1}	depolarized		
1905 cm^{-1}	polarized	axial stretch	A_1

The 1905 cm^{-1} band is partly polarized, while the 2027 cm^{-1} band is strongly polarized. This behavior corresponds to the depolarizations found[58] for the analogous monosubstituted octahedral complexes, $BrMn(CO)_5$ and $Ph_3SnRe(CO)_5$. The stretching mode of the CO trans to the ligand is slightly polarized, and the symmetric equatorial mode is strongly polarized.

This positive evidence for an E mode has an important consequence. It is evidence that the product is monosubstituted. Besides the structures considered above, there are other possibilities, which have more than one non-CO ligand. Edgell, et al., have discussed the representations of the CO stretching vibrations of various molecules having three to five CO's and one to three other ligands.[42] (Since the product has three CO stretching bands it must contain at least three CO's. No reasonable mononuclear metal carbonyl contains three CO's and more than three other ligands.) Of the structures that have an E mode, $LFe(CO)_5$, trans-$L_2Fe(CO)_4$, fac-$L_3Fe(CO)_3$, $Fe(CO)_5$, trans-$L_2Fe(CO)_3$, and axial-$LFe(CO)_4$, only one would have the observed pattern of CO stretching bands in the infrared and Raman spectra, axial-$LFe(CO)_4$.

What is the nature of the ligand, L? The bands in the middle frequency region of the infrared spectrum can shed considerable light on this question. Aside from the bands in the 2,000 cm^{-1} region, there are bands at 1586 cm^{-1} and 1413 cm^{-1} (THF solutions). These bands are much too high in frequency to be due to metal-carbon stretching or metal-carbon-oxygen bending modes, which absorb in the 785 to 300 cm^{-1} range. This leaves only the ligand moiety itself.

Carbonyl groups bridging two metal atoms have been observed[63] to have peaks in infrared spectra from 1898 to 1785 cm^{-1}. Clearly, the 1586 cm^{-1} band is far beyond this range. Furthermore, there is no evidence that requires a polynuclear species. The spectroscopic evidence, thoroughly explored above, unequivocally supports the mononuclear structure, $LFe(CO)_4$.

1586 cm^{-1} is a quite reasonable stretching frequency for a carbonyl bridging a metal and an organic group. The infrared spectra of diverse compounds containing an acyl or alkoxycarbonyl group have been reported. The following are some representative cases.

King and Bisnette have measured the infrared spectra of eleven acyl derivatives of cyclopentadienyl metal carbonyls.[64] The iron compounds have the general formula, $RCOM(CO)_2C_5H_5$, while the molybdenum and tungsten compounds have the formula, $RCOM(CO)_3C_5H_5$. The R substiuents included such varied groups as ethyl, phenyl, vinyl and triflouromethyl. All of these compounds have an acyl CO stretching band in the region of 1603 to 1659 cm^{-1}.

The acetyl carbonyl group of the octahedral manganese complexes, cis and trans $CH_3COMn(CO)_4P(C_6H_5)_3$ absorb at 1625 cm^{-1} and 1646 cm^{-1} respectively.[65] Finally, $Co(CO)_4COCF_3$ has its acetyl CO stretching vibration[66] at

1685 cm^{-1}.

As examples of alkoxycarbonyl derivatives there are the varied complexes listed in table 4. These have bridging CO stretching frequencies in the same region as the acyl complexes.

In summary, the CO bridging a metal atom and an alkyl or alkoxycarbonyl group absorbs in the fairly narrow range of about 1695 to 1600 cm^{-1}.

Although they are quite diverse, the above compounds have one aspect in common: they are all neutral. For an anionic complex, the stretching frequency of the acyl or alkoxycarbonyl C=O would be lowered by back donation just as the terminal CO stretching frequencies are. A drop of 50 to 100 cm^{-1} is not unreasonable. There are few anionic cases from which to generalize an absorption range, but the known complexes are close to the 1586 cm^{-1} value for the product. For example,[73] the acyl group of $CH_3COMnI(CO)_4^-$ absorbs at 1566 cm^{-1}. This is much lower than the corresponding band in the neutral acyl complex $CH_3COMn(CO)_5$, which appears at 1657 cm^{-1}.

The NMR spectrum of the product in THF consists of one peak, a singlet at δ 3.5 (downfield from TMS). Therefore, the ligand, L, must contain a proton, or several

TABLE 4

BRIDGING C=O STRETCHING FREQUENCIES OF THE ALKOXYCARBONYL GROUP OF NEUTRAL METAL CARBONYLS

Complex	Frequency	Reference
$CH_3C(=O)OFe(CO)(PPh_3)(C_5H_5)$	1630 cm^{-1}	67
$C_{10}H_{19}C(=O)OFe(CO)(PPh_3)(C_5H_5)$	1615 cm^{-1}	67
$CH_3C(=O)ORe(CO)_5$	1639 cm^{-1}	68
$C_2H_5C(=O)ORe(CO)_5$	1636 cm^{-1}	68
$CH_3C(=O)OFe(CO)_2(C_5H_5)$	1615 cm^{-1}	69
$CH_3C(=O)OMn(CO)(NO)(C_5H_5)$	1615 cm^{-1}	69
$(CH_3)_3C(=O)OCo(CO)_4$	1695 cm^{-1}	70
$CH_3C(=O)OIr(CO)_2(PPh_3)$	1655 cm^{-1}	71
$C_2H_5C(=O)OMn(CO)_5$	1644 cm^{-1}	72
$C_2H_5C(=O)OMn(CO)_3(PPh_3)_2$	1606 cm^{-1}	72
$CH_3C(=O)ORe(CO)_3(PPh_3)_2$	1613 cm^{-1}	72

protons in the same environment.

The ligand which bests fits the spectroscopic evidence is $-C(=O)OCH_3$ (figure 30). There are three equivalent protons. The chemical shift is close to that found for a methyl group attached to an oxygen atom in other metal carbonyl complexes. For example, the methyl protons of $Re(CO)_5C(=O)OCH_3$ and $C_5H_5Fe(CO)_2C(=O)OCH_3$ absorb at $\delta 3.6$ and $\delta 3.4$ respectively.[68,66] Furthermore, the only band in the infrared spectrum that remains to be assigned, the 1413 cm^{-1} band, is in the region of absorption of the CH_3 deformation mode.

The ligand has a carbonyl group bridging a metal atom with an organic group, as implied by the 1586 cm^{-1} band. The 1586 and 1413 bands disappear upon hydrolysis, when the $-C(=O)OCH_3$ group is replaced by a hydrogen atom. Other bands that might be anticipated for this ligand, such as C-O stretching, are undoubtedly buried under the corresponding bands of the solvents, CH_3OH and C_4H_8O. Finally, this is an asymmetric and fairly bulky ligand, one which could reasonably cause splitting of a degenerate CO stretching mode.

This ligand is in complete agreement with the chemical evidence as well, which indicates than an addition

Figure 30

Axial $(CO)_4FeC(=O)OCH_3^-$

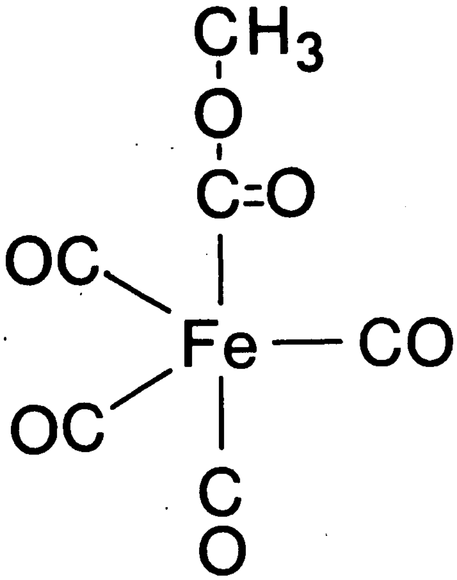


Figure 30

reaction takes place. Thus, the methoxide ion attacks one of the axial CO's of iron pentacarbonyl, forming the anion $(CO)_4FeC(=O)OCH_3^-$. The $-OCH_3$ structural unit maintains its integrity, allowing reversal of the reaction by simply cleaving the methoxide ion from the carbonyl group.

$$Fe(CO)_5 + OCH_3^- \rightleftharpoons (CO)_4FeC(=O)OCH_3^- \qquad (63)$$

The equilibrium constant of the reaction was calculated from the absorbance of equal initial concentration of iron pentacarbonyl in methanol, and in a 1:1 mixture with methoxide. It was found to be 1.2×10^2 $Lmole^{-1}$.

The percentage composition of the tetraphenylarsonium salt of the product agrees with that calculated for $(C_6H_5)_4As^+ \ Fe(CO)_4COOCH_3^-$. The percentages calculated for other possible salts do not fit as well. (See table 5.) The slightly high values found for carbon and hydrogen are probably due to some coprecipitation of $(C_6H_5)_4As^+OCH_3^-$.

In addition, $(CO)_4FeC(=O)OCH_3^-$ is in agreement with all that is known about the hydrolysis of the product. The reactions can be written:

$$Fe(CO)_5 + OCH_3^- \rightleftharpoons (CO)_4FeC(=O)OCH_3^- \qquad (64)$$

TABLE 5

PERCENT COMPOSITION OF TETRAPHENYLARSONIUM SALTS OF VARIOUS IRON CARBONYL ANIONS

	C	H	As	Fe
Ph_4As^+ Salt of First Product	59.38	3.87	11.82	8.79
Ph_4As^+ $(CO)_4FeCOOCH_3^-$	59.04	3.80	12.28	9.15
Ph_4As^+ $(CO)_4FeH^-$	60.90	3.83	13.57	10.11
Ph_4As^+ $(CO)_4FeCOCH_3^-$	60.63	3.90	12.61	9.39
$(Ph_4As^+)_2$ $(CO)_3Fe(COOCH_3)_2^{2-}$	64.67	4.53	14.62	5.45
Ph_4As^+ $(CO)_4FeCOOCH_3^- \cdot HOCH_3$	57.96	4.24	11.66	8.70

$$(CO)_4FeC(=O)OCH_3^- + H_2O \longrightarrow HFe(CO)_4^- + CH_3OC(=O)O^- + H^+ \qquad (65)$$

$$H^+ + OCH_3^- \longrightarrow HOCH_3 \qquad (66)$$

This scheme is consistent with all the observed species and preserves the mass balance of the reaction. Now the 1:2 stoichiometry is understandable. For every mole of iron pentacarbonyl, one mole of methoxide ion is needed to form the product and one mole is required in the hydrolysis. This second mole of OCH_3^- is always available because of the easy reversibility of reaction 64.

The lability of the methoxide group is clearly seen in the NMR spectra of methanol solutions. These spectra show only two singlets, one in the hydroxyl region and one in the methoxy region. The position of the peaks varies slightly with the concentration of methoxide and product. Obviously, there is rapid exchange of OCH_3^- among methanol, free methoxide ion, and $(CO)_4FeC(=O)OCH_3^-$.

This explains the appearance of $Fe(CO)_5$ upon hydrolysis of $(CO)_4FeC(=O)OCH_3^-$ in THF. Even though a 1:1 mixture goes far to completion in THF, there is always some free methoxide. Since a total of two moles of OCH_3^- are required per mole of $Fe(CO)_5$, one mole of iron pentacarbonyl must be left over.

$$(CO)_4FeC(=O)OCH_3^- + HOH \longrightarrow HFe(CO)_4^- + CH_3OC(=O)O^- + H^+ \qquad (67)$$

$$(CO)_4FeC(=O)OCH_3^- \rightleftharpoons Fe(CO)_5 + OCH_3^- \qquad (68)$$

$$OCH_3^- + H^+ \longrightarrow HOCH_3 \qquad (69)$$

The net equation is the following:

$$2(CO)_4FeC(=O)_3^- + HOH \longrightarrow HFe(CO)_4^- + CH_3OC(=O)O^- + Fe(CO)_5 + HOCH_3 \qquad (70)$$

Identification of the Second Product

The second product exists in equilibrium with the first, and forms when there is a large excess of methoxide ion. These facts imply that a second mole of methoxide attacks the $(CO)_4FeC(=O)OCH_3^-$ ion in an addition reaction.

The infrared spectrum of the second product in the carbonyl region consists of a single band at 1780 cm^{-1}. There are only two products with a single IR active CO stretching mode that could reasonably result from the above type of reaction.

The first possibility is that the methoxide ion attacks the carbonyl carbon of the ester group, presumably analogous to hydrolysis.

$$(CO)_4FeCOOCH_3^- + OCH_3^- \longrightarrow Fe(CO)_4^{2-} + CH_3OC(=O)OCH_3 \qquad (71)$$

Dimethylcarbonate splits off, leaving the known ion, tetracarbonatylferrate(II). This ion has one IR active CO stretching mode, the asymmetric mode, T_2.

The other possibility is that the methoxide ion attacks the other axial CO to give the disubstituted product, $(CO)_3Fe(COOCH_3)_2^{2-}$.

$$(CO)_4FeCOOCH_3^- + OCH_3^- \rightleftharpoons (CO)_3Fe(COOCH_3)_2^{2-} \qquad (72)$$

This diaxial species has one IR active CO stretching mode, the asymmetric stretching of the equatorial CO's, E'.

Both possibilities fulfill the additional requirement that the second product be dinegative. The second product band is about 100 cm^{-1} lower than the bands of the first product. Therefore, there must be significantly greater negative charge on this product than on the first.

The first possibility, $Fe(CO)_4^{2-}$, is untenable while the second, $(CO)_3Fe(COOCH_3)_2^{2-}$, is supported for several reasons. First, the 1780 cm^{-1} band has a shoulder centered at about 1815 cm^{-1}. The CO stretching mode of $Fe(CO)_4^{2-}$, though degenerate, is not expected to be split. On the other hand, the disubstituted product has two unsymmetric ligands. It could reasonably give a band with a shoulder, especially in view of the broad band found for the E mode of the monosubstituted first product (methanol solutions).

A solution of $Fe(CO)_4^{2-}$ was prepared in methanol in the manner given in the literature for aqueous solutions. 0.40 ml of $Fe(CO)_5$ was stirred overnight in a 3.4 M solution of KOH in methanol. The band of $Fe(CO)_4^{2-}$ is located at 1775 cm^{-1}. However, it does not have a shoulder (figure 31). It also differs in shape from the band of the second product, being rounded at the peak.

Secondly, it is difficult to see how reaction 71 would be reversed by the addition of methanol. On the other hand, dilution would be expected to shift the equilibrium of reaction 72 to the right by favoring the dissociation of product over association of reactants.

Thirdly, solutions of the second product were carefully examined for the presence of dimethylcarbonate. If a 3% solution of dimethylcarbonate im methanol is extracted with hexane, the bands of dimethylcarbonate are clearly visible in the infrared spectrum of the hexane. But when a solution of the second product, of such concentration that

Figure 31

Infrared spectrum of $Fe(CO)_4^{2-}$ in methanol

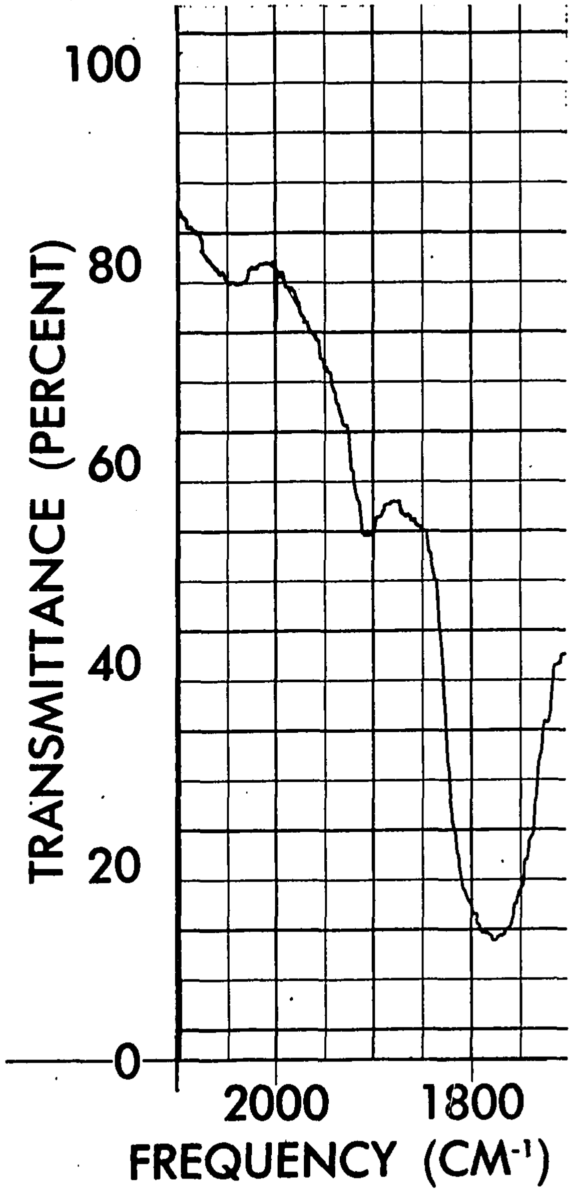

100
80
60
40
20
0
TRANSMITTANCE (PERCENT)
2000
1800
FREQUENCY (CM⁻¹)

Figure 31

it should contain about 10% dimethylcarbonate, is extracted, no bands appear other than those of hexane.

Proton NMR spectra of solutions of the second product were searched for the singlet of dimethylcarbonate. Although the peak could be seen in solutions prepared with as little as 1% $CH_3OC(=O)OCH_3$, none could be detected in much more concentrated solutions of the second product.

The conclusion is clear. The second product is the disubstituted species, $(CO)_3Fe(COOCH_3)_2{}^{2-}$. The equilibrium constant for equation 72 was calculated using the absorbances of infrared bands. It was found to be 6.7×10^{-1} L mole^{-1}.

There is an interesting corroboration of this result. Brunner and Schmidt[67] found inversion of configuration for the transesterification of the tetrahedral complexes, (+) and (-) $C_5H_5Fe(COOC_{10}H_{19})(CO)(PPH_3)$, but retention of configuration upon transesterification of (+) and (-) $C_5H_5Fe(COOC_{10}H_{19})(NO)(PPh_3)$. From this they derive the order of reactivity toward nucleophilic attack: $CO > COOR > NO$. This is what is observed for the formation of the second product. The methoxide ion attacks not at the ester carbonyl carbon (equation 71), but at the carbonyl carbon (equation 72).

Before leaving this topic it is worth mentioning an experiment that did not give conclusive results. It was thought that positive evidence for the disubstituted product could be obtained from the ^{1}H-NMR spectrum of a solution containing $(CO)_4FeCOOCH_3^-$ (1:7), and of a solution of $(CO)FeCOOCH_3^-$ and $(CO)_3Fe(COOCH_3)_2^{2-}$ (1:14.5). The presence of still another species exchanging OCH_3^-, ie., the second product, should cause a detectable shift in the peak of the methoxy protons. Finding such a shift is positive evidence that the second product contains protons, protons that are in a different environment from those of $(CO)_4FeCOOCH_3^-$. As can be seen from table 3, the shift due to the presence of the first product, and that due to the second are too small to be useful. Decreasing the concentration of methoxide ion by about half causes a 5 Hz upfield shift of the methyl proton peak, from 207 Hz to 202 Hz. A solution of the first product has a methyl proton peak at 203 Hz and the solution of both products has this peak at 207 Hz. That is, the changes are only a few Hz.

This apparently stems from two facts. The position of an NMR peak, resulting from exchanging species, depends on the concentration of the species and on the difference between their chemical shifts. For the products both of these are small. Indeed, the largest effect is due to the changes in concentration of the methoxide ion. Thus, adding the products to a solution of methoxide in methanol has too small an effect on the peak position to give reliable evidence.

Some Further Properties of the Solutions

The effect of adding water to a methanol solution of $(CO)_4FeCOOCH_3^-$ and $(CO)_3Fe(COOCH_3)_2^{2-}$ was described in the Experimental section. It was stated that the 1780 cm^{-1} band, originally due to the second product, became more intense and lost its shoulder. The reason for this is the following: as the solution was hydrolyzed to $HFe(CO)_4^-$, the hydridotetracarbonylferrate ion reacted with the OCH_3^- present in the solution to give $Fe(CO)_4^{2-}$. The broad bands of $(CO)_3Fe(COOCH_3)_2^{2-}$ and $Fe(CO)_4^{2-}$ are coincident. Hence, as the former lost intensity and the latter grew in, the band resulting from their overlap appeared to change shape and intensity.

A methanol solution of the products (1:14.5) was heated by immersion in an oil bath. Three hours of heating at 70° produced no new products. The only effect was a shift in the position of equilibrium of reaction 72 toward the right, ie., the concentration of $(CO)_3Fe(COOCH_3)_2^{2-}$ increased at the expense of $(CO)_4FeCOOCH_3^-$ as seen by the intensity of their infrared bands. Therefore, formation of the second product is endothermic.

The absence of new products upon heating is in contrast to the amide substituted iron tetracarbonyls. (See Introduction.) Over a period of several days, or more quickly with heating at 60°, these produce carbon monoxide, which comes off as a gas or reacts with excess amine. The complex becomes an amine substituted iron tetracarbonyl. That $(CO)_4FeC(=O)OCH_3^-$ does not undergo an analogous reaction is probably due to instability of the expected product, $(CO)_4FeOCH_3^-$.

Also in contrast is the fact that amide substituted iron tetracarbonyl does not react with excess amine to give a disubstituted product. It is likely that the methoxide ion gives disubstitution because of its relatively greater basicity.

Conclusion

The iron pentacarbonyl-methoxide reaction has been shown to proceed by the carbonyl insertion mechanism, in which the initial step is the attack of the base on a carbonyl carbon.

The other known reactions of iron pentacarbonyl with bases under mild conditions can be seen to proceed by this mechanism. Iron pentacarbonyl and saturated amines have already been shown to react by the carbonyl insertion mechanism.[42,43]

Although the iron pentacarbonyl-hydroxide reaction, which takes place in aqueous solution, may not appear to fit the pattern, it can be understood as proceeding by a carbonyl insertion immediately followed by hydrolysis.

$$Fe(CO)_5 + OH^- \longrightarrow (CO)_4FeC(=O)OH^- \qquad (73)$$

$$(CO)_4FeC(=O)OH^- + HOH \longrightarrow (CO)_4FeH^- + HOC(=O)OH \qquad (74)$$

$$HOC(=O)OH + 2\ OH^- \longrightarrow 2HOH + CO_3^{2-} \qquad (75)$$

Treatment with liquid ammonia for 14 days reduces $Fe(CO)_5$ to $Fe(CO)_4^{2-}$. Urea and ammonium ion are also produced.[12] This reaction, too, can be understood as proceeding in a manner analogous to the iron pentacarbonyl-hydroxide reaction. In this case liquid ammonia is the base as well as the solvent. The second step is ammonolysis instead of hydrolysis. Urea is the counterpart of the carbonate formed in the hydroxide reaction.

$$Fe(CO)_5 + NH_3 \longrightarrow (CO)_4FeC(=O)NH_3 \qquad (76)$$

$$(CO)_4FeC(=O)NH_3 + NH_3 \longrightarrow (CO)_4FeH^- + H_2NC(=O)NH_2 + H^+ \qquad (77)$$

$$(CO)_4FeH^- + NH_3 \longrightarrow (CO)_4Fe^{2-} + NH_4^+ \qquad (78)$$

$$H^+ + NH_3 \longrightarrow NH_4^+ \qquad (79)$$

These equations give the overall reaction:

$$Fe(CO)_5 + 3NH_3 \longrightarrow (CO)_4Fe^{2-} + NH_4^+ + H_2NC(=O)NH_2 \qquad (80)$$

Thus, the initial step in the reaction of iron pentacarbonyl with bases is the attack of the base on a carbonyl carbon. This reaction pathway has been demonstrated for the iron pentacarbonyl-methoxide and iron pentacarbonyl-amine reactions. It is also the most satisfactory explaination for the iron pentacarbonyl-hydroxide and iron pentacarbonyl-liquid ammonia reactions. Therefore, it can be concluded that the carbonyl insertion mechanism is a general one for iron pentacarbonyl-base reactions under mild conditions.

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